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ON
The Conduction of Electricity in Solids

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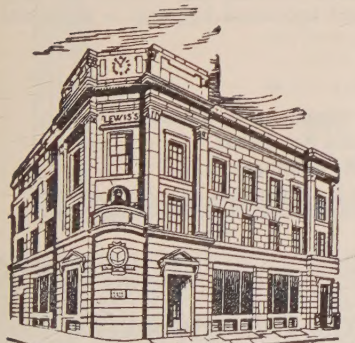

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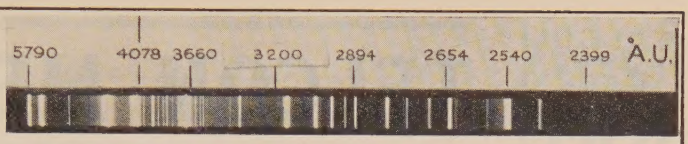

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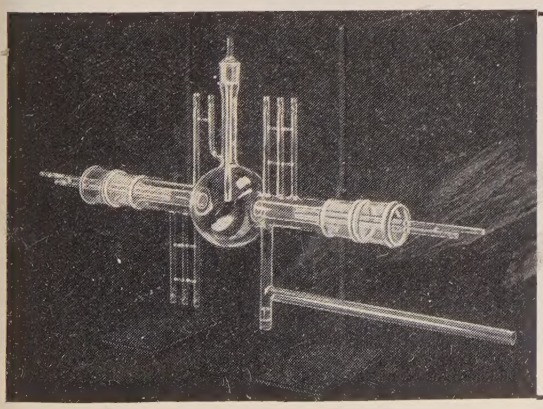

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THE CONDUCTION OF ELECTRICITY IN SOLIDS

Report of the
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INTRODUCTION

By N. F. MOTT

ELECTRICITY may be carried in solids and liquids either by charged ions (electrolytic conduction) or by electrons. The papers in the present volume are concerned almost entirely with the conduction due to electrons. The first group of papers deals with conduction in insulators and semi-conductors, that is to say in solids in which there are normally at low temperatures no free electrons. They can only conduct if electrons are freed, either by irradiating the solid with light of a frequency which it can absorb, thus releasing electrons by a kind of internal photoelectric effect, or in the case of semi-conductors by keeping the solid at not too low a temperature, so that the thermal agitation of the atoms of the solid is able to free a few electrons.

The first paper is by R. W. Pohl, whose school in Göttingen has been for many years investigating photoconductivity in the alkali halides. These crystals do *not* show photoconductivity if they are illuminated in their own characteristic absorption band; in order to obtain photoconductivity one must first colour the crystal by the addition of some impurity or defect, which gives a new absorption band. The crystals used by Pohl are coloured by heating in the vapour of the alkali metal, which gives the well-known yellow colour of rock salt crystals or blue of KCl. The crystal shows photoconductivity if irradiated in the new absorption band so obtained. This band is known as the F band and the absorbing centres as F centres; their precise origin is at present uncertain, though hypotheses to explain it are advanced in the papers by Gurney and Mott and in the subsequent discussion.

An electron released from an F centre by the absorption of a quantum of radiation travels through the crystal only a certain distance before it is trapped, apparently in a less stable position called an F' centre. Thermal motion may release it, but it does not necessarily form another stable F centre until minutes or hours have elapsed. This suggests at once a mechanism for phosphorescence in crystal phosphors, on which we publish papers by R. Hilsch and by J. T. Randall. In the sulphide phosphors made by the addition of a heavy metal, it is possible that an electron is ejected from an impurity atom, forms an F' centre or something of the kind a long way off, and only re-radiates when it finds the parent atom again some time later. This hypothesis is supported by the temperature-dependence discussed by Randall, but cannot be applied to the alkali halides.

In semi-conductors free electrons are released, not by the absorption of light but by thermal agitation. In the theory given by Wilson in 1931 it is suggested

that the electrons are released from impurities and defects; according to this theory the conductivity should be given by a law of the type $\sigma = Ae^{-E/kT}$. In the paper on semi-conductors by J. H. de Boer it is shown that experiment is in disagreement with theory in a number of ways. First, the parameter E depends often on the concentration of the impurity; and, secondly, there exists a number of semi-conductors which, according to the theory, ought not to be semi-conductors at all, but metallic conductors. These are ionic crystals with incomplete d shells, such as NiO. In the discussion of de Boer's paper, R. Peierls suggests that quite a drastic modification of the present electron theory of metals will be necessary if it is to include these substances.

The second group of papers deals with conduction in metals. Both on the experimental and on the theoretical side the study of conduction in metals is much further advanced than in insulators; so that, whereas in the latter case a host of problems remains to be investigated in connexion with the problem of conduction in the simplest substance, sodium chloride, in the case of metals we deal with problems of a more special nature.

G. Borelius gives an account of the work carried out by his school at the Technical College, Stockholm. This deals mostly with the magnetic and electrical properties of alloys and shows very clearly how the resistance is increased by the addition of any impurity which enters into solid solution, and also how the resistance is intimately related to the magnetism. Of especial interest is his account of alloys in which a superlattice can be formed, and his complete description from the point of view of thermodynamics of the transition between the ordered and disordered states.

W. L. Bragg describes his more recent attempt to obtain an atomic picture of the process, and the work carried out at the University of Manchester and at the laboratories of Metropolitan-Vickers by A. H. Bradley and C. Sykes. In this work again the conductivity and hence the mean free path are always found to be less in the disordered than in the ordered state.

C. H. Desch describes age-hardening alloys with especial reference to their resistance; the mechanism by which atoms in a supersaturated solid solution crystallize out is discussed.

The conduction of electricity in thin metallic films has been the object of a very large number of investigations. In an introductory paper G. I. Finch gives an account of the structure of such films as revealed by electron diffraction. E. T. S. Appleyard describes recent work by Lovell carried out under his direction in which apparently uniform layers of alkali metal are deposited on glass, and which, with a thickness of five or six atomic layers, have a resistance only about ten times greater than that of the bulk metal. The mechanism of conduction in so thin a film is discussed. In other metals (e.g. mercury) islands of metal seem to be formed, and the mechanism by which this can occur is outlined by J. E. Lennard-Jones. The different electrical properties that films of metal can have, according to their past history, is well brought out in the papers by A. Féry and J. Bernamont.

Finally a few words must be said about the account of the discussions published in this volume. This has been prepared by members of the staff of the Physics Department of the University of Bristol, who must take responsibility for the opinions expressed, since in the interests of speed of publication these summaries have not in all cases been submitted to the original speakers. No attempt has been made to include everything that was said; on the other hand, in certain cases remarks made in private discussion after the meetings have been included.

PART I

CONDUCTION IN NON-METALS

ELECTRON CONDUCTIVITY AND PHOTOCHEMICAL PROCESSES IN ALKALI-HALIDE CRYSTALS

By R. W. POHL, Göttingen

§1. INTRODUCTION

The fact that electrons can move about in the interior of highly insulating crystals was first definitely established in the case of the diamond[87]. If a diamond crystal is placed in series with a battery of several hundred volts and a sensitive galvanometer, electron currents of the order of 10^{-9} A. may be observed upon illuminating the crystal with the light of a match. The number of crystals showing similar properties increased rapidly, but the observations continued to be generally of a qualitative nature. To be sure, it soon became evident that this phenomenon was related to photochemical processes, fluorescence and phosphorescence.

Quantitative measurements could be expected as soon as it became possible to work with artificially-produced crystals of well-defined chemical constitution. A series of preliminary experiments showed that this condition could be most simply fulfilled in crystals of the alkali halides. These can be produced with a high degree of chemical purity from fused salts. Single crystals of the size of an apple, or even having a content of a litre are relatively easily obtainable[9,41]. With the help of crystals so produced, the phenomena of electron conductivity and photochemical processes have been quite satisfactorily explained. The following report presents the most important results of the work, not a history of the individual problems. The investigations concerning fluorescence and phosphorescence processes are still in their initial stages, and will therefore not be included in this report, which is divided into the following four parts:

Part 1. The optical properties of the alkali-halide crystals in their pure state as well as when containing a stoichiometric excess of one of the components, i.e. either alkali metal or halogen (§§ 2–6).

Part 2. The motion of electrons released in the interior of these crystals through light, or more briefly: photoelectric currents in the crystals (§ 7).

Part 3. The motion of electrons thermally released, and the connexion between electron conductivity and ionic conductivity (§§ 8–9).

Part 4. Photochemical processes in the crystals (§§ 10–12).

Until 1926 these investigations were made jointly with B. Gudden (Gudden is now Professor of Physics at the University of Erlangen) and in later years with Dr Hilsch (now first assistant in my institute in Göttingen). Among numerous co-workers I should like to mention particularly: Z. Gyulai, E. Mollwo, A. Smakula, O. Stasiw, and recently G. Glaser, W. Lehfeldt, H. Pick and E. Rögener.

PART 1. THE OPTICAL PROPERTIES OF THE ALKALI-HALIDE CRYSTALS

§2. THE OPTICAL PROPERTIES OF PURE ALKALIDE CRYSTALS.

The alkali-halide crystals, with their cubic lattice composed of positive and negative ions, probably represent the simplest type of solid body. They are perfectly transparent throughout a spectral range of almost six octaves and have a smooth dispersion curve, as illustrated in figure 1 for the case of LiF[16,28,41,79].

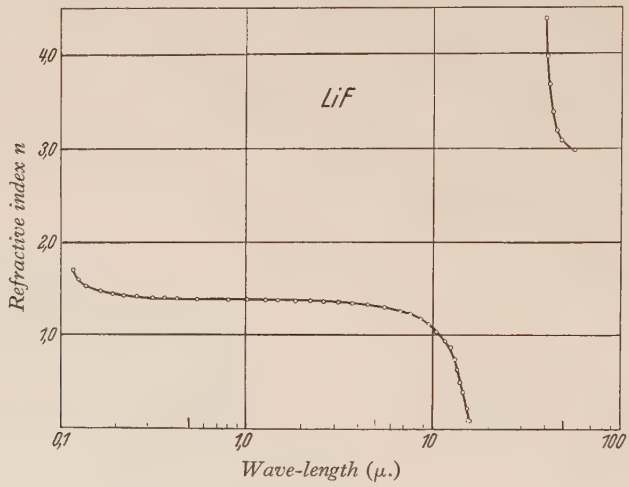


Figure 1.

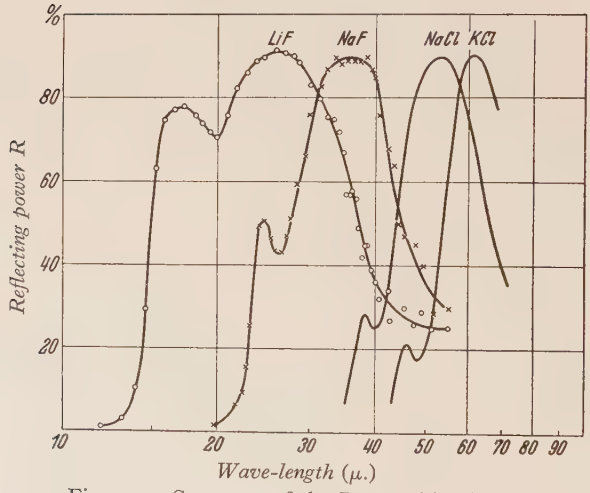
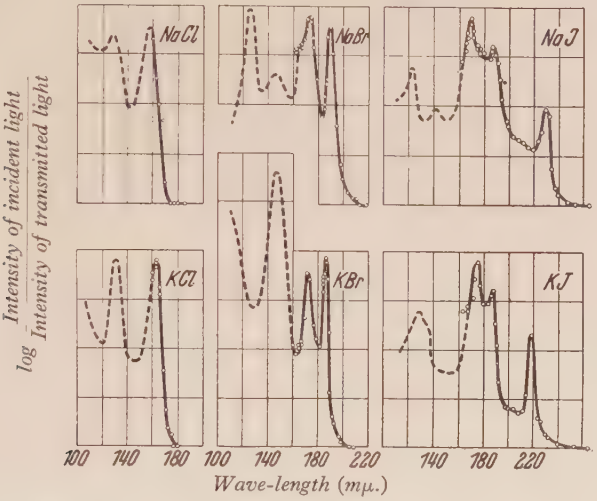


Figure 2. Structure of the Reststrahlen bands.

The rapid decrease of the index of refraction in the infra-red begins as soon as the region of residual rays (*Reststrahlen*), i.e. ionic vibrations, is reached. The structure of the residual ray bands is not as simple as supposed by their discoverer, Heinrich Rubens. Figure 2 gives typical curves for four salts[37,79]. The values of the

absorption constants in the infra-red have been determined only for a limited range of wave-lengths. The measurements hitherto made do not suffice for a diagram.

In the ultra-violet, the state of affairs is quite different. There the absorption spectra, which cause the rapid increase of the index of refraction in the region of short waves, have been carefully measured[20, 23, 27]. Figure 3 shows the absorption spectra of three Na salts and figure 4 of three K salts, which have recently been extended by the measurements of Schneider and O'Bryan[88]. The similarity of spectra lying above one another is to be noticed.



Figures 3 and 4. Ultraviolet absorption of crystals.

The absorption constant K defined by the equation

$$J_d = J_0 e^{-Kd} \qquad \ldots\ldots(1),$$

where J_0 is the intensity of the entering light, J_d the intensity of the transmitted light, and d the thickness of the specimen, has been measured for the first absorption bands of several salts in the form of thin films of thickness[49, 53] 2 to $10 \cdot 10^{-6}$ cm. These are given in table 1. In order to facilitate comparison with the absorption of light in metals, the values of the absorption coefficient $n\kappa$, defined by the equation

$$J_d = J_0 e^{-4\pi (n\kappa)\, d/\lambda_{air}} \qquad \ldots\ldots(2),$$

have also been calculated, and are given in col. 4. The fifth column gives the molecular absorption constant β, defined by the equation

$$J_d = J_e \cdot e^{-\beta N/F} \qquad \ldots\ldots(3).$$

Here N is the number of molecules under the surface F and β represents the absorbing cross-section of the individual molecules for the incident photons.

These data are for crystals of the highest chemical purity obtainable. In experiments dealing with electronic conductivity, photochemical processes and luminescence phenomena, the starting material, if possible, should contain no more

than one foreign molecule in 10^5 to 10^6 halide molecules. Greater concentrations of foreign molecules cause disturbances and the appearance of secondary effects [15, 45].

Table 1. Absorption in the first ultra-violet absorption band

Crystal	Wave-length of the band ($m\mu$.)	Absorption constant K ($cm.^{-1} \times 10^5$)	Absorption coefficient $n\kappa$	Molecular absorption constant β ($cm^2 \times 10^{-17}$)
NaBr	192	10·0	1·53	5·5
KBr	189	8·8	1·33	6·3
RbBr	193	7·0	1·07	5·6
KJ	220	7·2	1·26	6·3
RbJ	223	7·0	1·24	6·9

Moreover, for a complete investigation it is necessary to know in addition to the optical properties of the pure crystals the changes which are introduced when small deviations occur in the stoichiometric composition of the crystals. It is possible to produce crystals with a small excess of alkali metal or of halogen.

§3. PRODUCTION OF ALKALI-HALIDE CRYSTALS WITH A STOICHIOMETRIC EXCESS OF ALKALI METAL

If an alkali-halide crystal is heated in the vapour of its cation metal, a stoichiometric excess of alkali metal is produced in the interior of the crystal, which imparts a bright colour to the crystal. In the simplest case this colour is caused by neutral alkali atoms which are loosely bound in the interior of the crystals in some manner or other. These foreign atoms shall be designated by the name *Farbzentren* (colour centres). The absorption spectrum has the form of a simple bell curve such as is shown in figure 5 for the five alkali-chloride crystals [18, 60].

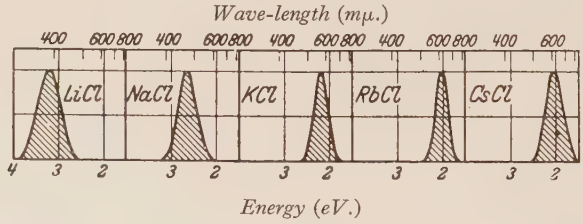


Figure 5. Absorption bands of the Farbzentren at 20° C.

The number of Farbzentren can be determined from the magnitude of the absorption constants and the half-width of the bands. The details of this calculation will be given in § 4.

The number of Farbzentren per $cm.^3$ of the crystal is proportional to the number of metal atoms per $cm.^3$ in the vapour surrounding the crystal [42]. Figure 6 shows this fact for the case of KBr [80]. In making these measurements, the vapour pressure of the metallic vapour and the temperature of the crystal could be varied independently of one another. The ratio

$$\alpha = \frac{\text{number of Farbzentren per cm.}^3}{\text{number of vapour atoms per cm.}^3}$$

is always greater than unity. Besides this, α decreases with increasing temperature of the crystal (see figure 7).

The binding of the Farbzentren may be described formally as a solution of alkali metals in the interior of the crystal. The law of mass-action may be applied and the

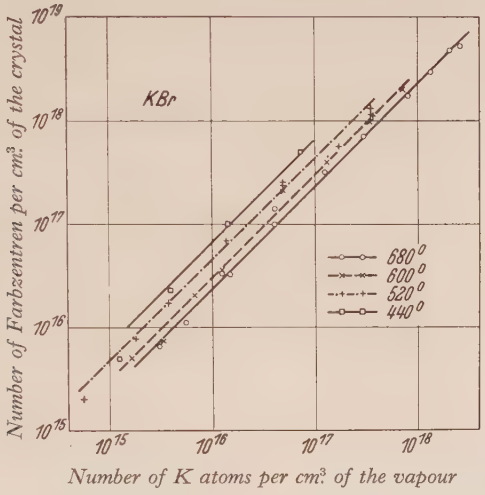


Figure 6. Solubility of K in a KBr crystal.

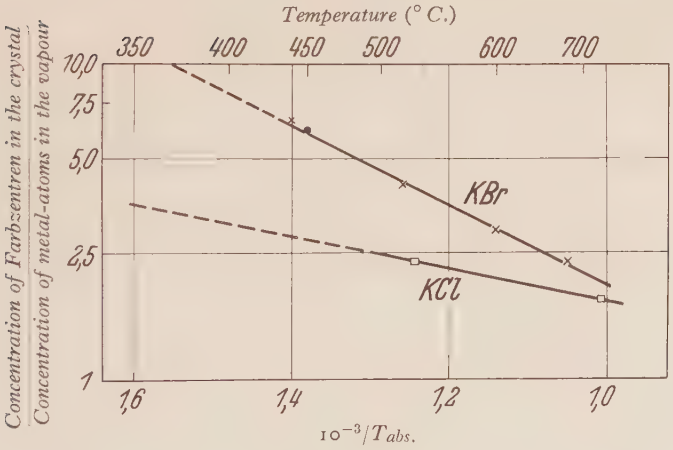


Figure 7.

constancy of the factor α would then mean that the process takes place without any change in the mol-number of molecules. This may be written as

$$K \text{ (in vapour)} \rightleftarrows K \text{ (in crystal)}.$$

According to this conception, the temperature dependence of the proportionality

factor α may be considered as consequence of a positive binding energy W_F, according to the equation

$$\frac{d(\log \alpha)}{d(1/T)} = \frac{W_F}{k} \qquad \ldots\ldots(4).$$

($k = 1{,}37 \cdot 10^{-23}$ watt-sec./° C.)

The binding energy W_F calculated by means of equation (4) from figure 6 gives the value $W_F = 0{\cdot}25$ eV. for the Farbzentren in KBr crystals, and from analogous measurements the value for the Farbzentren in KCl crystals is $W_F = 0{\cdot}10$ eV.[80]. Measurements on the other salts are still in progress.

Just how this process of the introduction of extra atoms into the crystal lattice, here formally described as "solution" takes place, remains uncertain. It may be due to inner absorption processes[7,8,11]. According to the experiments, as the temperature increases, the number of Farbzentren per cm^3 of the crystal approaches that of the atoms per cm^3 in the vapour[80].—As the melting-point of the crystal is passed, a new effect enters: Liquid KBr just above the melting-point is able to take up approximately 15 times as many alkali atoms per cm^3 as are present per cm^3 in the vapour[66].

Extrapolation of figure 7 down to room temperature 20° C., yields $\alpha_{KBr} = 3{,}6 \cdot 10^4$ and $\alpha_{KCl} = 9 \cdot 10^1$. Furthermore if the vapour-pressure curve for potassium is extrapolated to this same temperature, the resulting number of atoms per cm^3 is $7{,}5 \cdot 10^8$, and hence the equilibrium-concentration of Farbzentren in the crystal is

$$\left.\begin{aligned} c_{20°} &= 3 \cdot 10^{13} \text{ cm}^{-3} \text{ for KBr} \\ c_{20°} &= 7 \cdot 10^{10} \text{ cm}^{-3} \text{ for KCl} \end{aligned}\right\} \qquad \ldots\ldots(5).$$

These figures are to be considered merely as rough approximations, which indicate simply the order of magnitude. Moreover, an important practical conclusion can be drawn from them: in making experiments upon electron conduction and photochemical processes concentrations of Farbzentren below 10^{15} per cm^3 can rarely be used. Otherwise crystals of great thickness are necessary in order to obtain a measurable light absorption.* Accordingly in order to have enough absorbing centres to work with at room temperature it is practically always necessary to use a quenched crystal previously filled with Farbzentren at a high temperature, whose higher concentration can be preserved in this way. In so doing it is unavoidable that a fraction, albeit a very small fraction in most cases, of the excess of alkali metal atoms combine to form larger colloidal particles, which are precipitated as foreign bodies[11]. The absorption spectra of these colloids are very markedly affected by the particle size[32]. In individual cases, where these colloids introduce secondary effects, they must be measured and considered. Fortunately, however, in most cases colloid formation can be so far suppressed as to be negligible.

* 10^{15} Farbzentren per cm^3 of KCl, for example, produce (at room temperature) an absorption constant of 0·22 cm^{-1}; i.e. the light traversing the crystal must pass through a thickness of 4·5 cm. in order to be reduced to $1/e$ or 37 per cent of its original intensity.

§4. THE OPTICAL PROPERTIES OF THE FARBZENTREN

The absorption spectrum of the Farbzentren has a simple bell-shaped band, as was shown in figure 5. The form of this band is practically the same for all salts at the same temperature, as indicated in figure 8. In this figure[42] the curves obtained for the four salts have been reduced to the same abscissae by division by the proper frequency $\nu_0 = \nu_{max.}$. The curve drawn is that calculated on the basis of classical dispersion theory.

The form of the absorption spectra agrees well with the classical dispersion theory. The number N_0 of Farbzentren per unit volume[22], calculated on the basis of this theory, gives the equation

$$N_0 = 1{,}31 \cdot 10^{17} \frac{n_0}{(n_0^2+2)^2} . K_{max.} H \qquad \ldots\ldots(6),$$

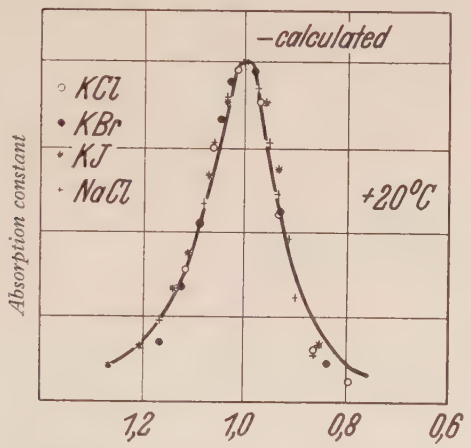


Figure 8.

where n_0 is the index of refraction of the crystal for the same wave-length of the band-maximum, $K_{max.}$ the absorption constant for the band-maximum in $cm.^{-1}$ according to equation (1), and H the half-width of the band in eV. This agrees very well with experiments. This equation may be written more simply

$$N_0 = A . K_{max.} . H \qquad \ldots\ldots(7).$$

The constant A, calculated on the basis of the theory for all halide crystals, has the average value of 10^{16}/eV. $cm.^2$. Moreover, for KCl the constant A determined from an analytical chemical measurement[75] has the value $A = 1{,}31 \cdot 10^{16}$/eV. $cm.^2$*

The position and the form of the absorption spectra change decidedly with temperature[6, 10]. As an example figure 9 shows measurements for KBr. A particular wave-length λ_0 is shown by a broken line. For each temperature this marks the point

* If all the Farbzentren have been coagulated into small colloid particles, the absorption band changes in both shape and location. In spite of this fact, equation (7) may be used in making estimations, and at least gives values of the right order of magnitude[40].

on the violet side of the absorption band at which the absorption-constant K has dropped to half the value of $K_{max.}$. This wave-length has the same position for all

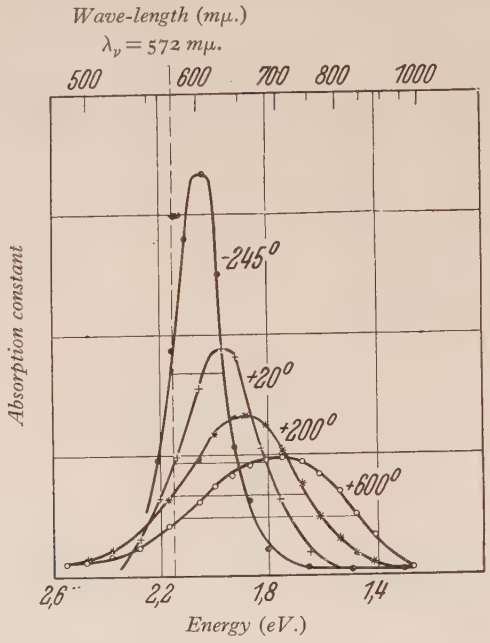


Figure 9. Absorption band of Farbzentren in KBr.

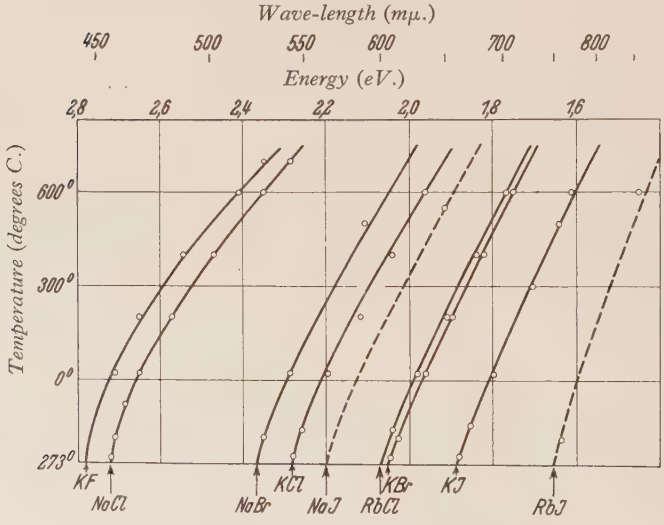


Figure 10. Absorption-band maxima of the Farbzentren.

temperatures[42]. This may possibly be ascribed to a transition between two undisturbed energy levels of the crystal. Further, figure 10 shows the position of the band-maximum for nine different crystals as a function of the temperature. For any

particular temperature there is a close connexion between the frequency ν_0 of the band-maximum and the lattice-constant d of the crystal under observation[30]. At room temperature, the following relation is found to hold with close approximation

$$\nu_0 d^2 = 5 \cdot 10^{-5} \text{ sec}^{-1} \text{ m}^2 \qquad \ldots\ldots(8).$$

§5. THE OPTICAL EXCITATION OF FARBZENTREN

By the process of light absorption the Farbzentren disappear and in their place there appear new centres, somewhat more loosely bound, which will be called F' centres. Their absorption spectrum extends further into the region of long wave-lengths, and the maximum also is shifted in this direction[4, 29]. In favourable cases, the two maxima can be distinctly observed, as in figure 11. Curve A shows the absorption spectrum of the F centres before and curve B after excitation, i.e. after

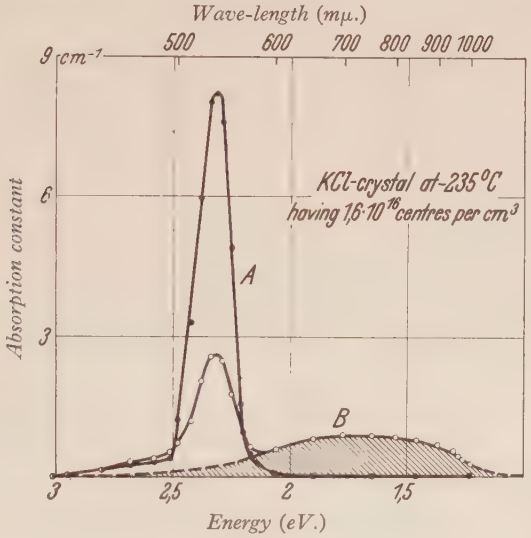


Figure 11.

irradiation by light which was absorbed by the F centres. The excitation took place at $-100°$ C. On the contrary, both spectra, A as well as B, were made at $-235°$ C., in order to make the band as narrow as possible and thus to separate them distinctly. As a result of the excitation, the F band has been reduced by about two-thirds and in its place the shaded absorption band of the F' centres appears[86]. These F' centres are stable only at low temperatures; they have only a limited life at higher temperatures[14], being changed back into F centres by thermal motion. At 250° these F' centres could not exist longer than one second in any crystal.

Light absorption by F' centres, i.e. that of wave-length longer than 700 mμ. (as shown in figure 11) has the same effect as thermal motion. The transition $F \rightarrow F'$ is thus reversible[1]. The quantum yield of the transformation $F \rightarrow F'$ has

been measured repeatedly[3,22,86] but the investigations are not as yet completed. The ratio

$$\eta^* = \frac{\text{number of disappearing Farbzentren}}{\text{number of absorbed light quanta}}$$

is easily measured. More difficult, however, is the measurement of the ratio

$$\eta = \frac{\text{number of } F' \text{ centres formed}}{\text{number of absorbed light quanta}} \qquad \ldots\ldots(9).$$

For temperatures down to $-130°$ C., $\eta = \eta^*$, but at still lower temperatures it has been possible to measure only η^*, and this has been found to have a value of approximately unity down to $-200°$ C. (Individual values between 0·4 and 1·6: the reason for this variation is still unknown.) Measurements of η at temperatures below $-150°$ C. have not as yet been successful. This is connected with another

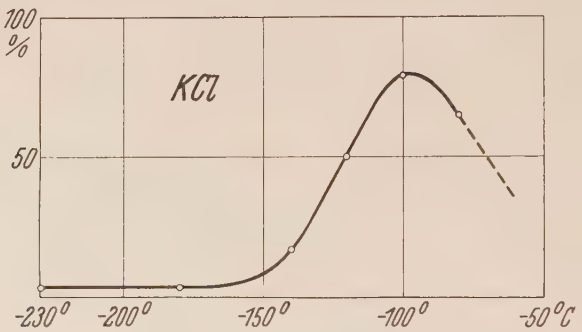


Figure 12. Ratio of decrease in number of Farbzentren due to excitation to number before excitation.

fact, also as yet unexplained: the number of disappearing Farbzentren is only initially proportional to the number of absorbed light quanta, but later approaches a saturation value. Only a fraction of the Farbzentren can be made to disappear by light absorption and this fraction is strongly dependent upon the temperature. Figure 12 shows an example of this, for the case of KCl. Principally noteworthy is the decrease in the direction of lower temperatures. The decrease towards higher temperatures is due simply to the experimental conditions. Here F' centres are produced by the disappearing Farbzentren, and the life of the F' centres is very short. By the time that the optical measurement of the number of centres has begun, a part of these F' centres has again disappeared. Further questions connected with figure 12 still need to be thoroughly investigated.

Note added in proof. Some new results are shown in figure 12 (*a*). The quantum yield for the $F \rightarrow F'$ transition begins at higher temperatures with the limiting value 2 and, as the temperature is lowered, falls much below 1; the dependence on temperature is much the same as for photochemical transitions (§ 12).

One light quantum can move only *one* electron; the latter can in the limiting case cause two Farbzentren to disappear and produce in their stead two F' centres.

The Farbzentren thus serve not only as sources of electrons, but their presence in the lattice also limits the range of the free electrons. An electron is ejected by a light quantum from a Farbzentrum and leaves in its place a positive alkali ion. The electron then diffuses in the electric field, and at the end of a finite range w is captured by a positive ion in the neighbourhood of another Farbzentrum. Thus it forms a new alkali atom. Both the neighbouring alkali atoms (which are in a region

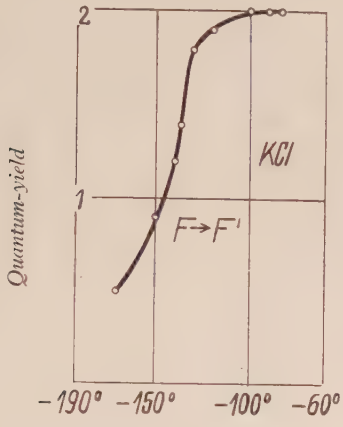


Figure 12 (*a*).

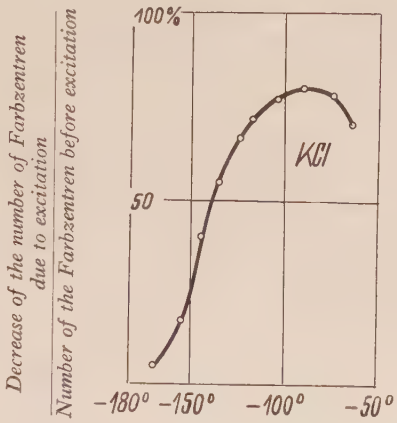


Figure 12 (*b*).

of superfluous negative charge) have an absorption spectrum somewhat different from that of two single Farbzentren, and appear optically in the form of two F' centres.

Figure 12 (*b*) shows newer measurements of the effect shown in figure 12.

The fact mentioned at the end of § 5 can be explained as follows: The quantum yield of the transition $F \rightarrow F'$ decreases with decreasing temperature, whilst the quantum yield of the transition $F' \rightarrow F$ retains its initial value. The equilibrium is thus displaced to the disadvantage of the F' centres.

§6. PRODUCTION AND OPTICAL PROPERTIES OF CRYSTALS WITH AN EXCESS OF HALOGEN

If an alkali-halide crystal is heated in the vapour of its halogen, a stoichiometric excess of halogen is formed in the interior of the crystal. This imparts a yellowish colour to the iodide and bromide crystals. Two absorption spectra[61,83] for this case are shown in figure 13. The number of halogen atoms which have penetrated into the crystal can be determined from the maxima I and II* (the third maximum is due to a secondary effect, see below).

* Equation (8) is applied to both maxima, and the constant A is determined by an electrical method to be described later on. For iodine equation (6) may also be used.

The number of halogen atoms per cm² of the crystal is proportional to the number of halogen molecules per cm² in the surrounding vapour[83]. Figure 14 shows this for KBr as an example. In these experiments the temperature of the crystal and the vapour pressure could again be varied independently of one another. The relation

$$\gamma = \frac{\text{number of halogen atoms per cm}^3 \text{ of the crystal}}{\text{number of halogen atoms per cm}^3 \text{ of the vapour}}$$

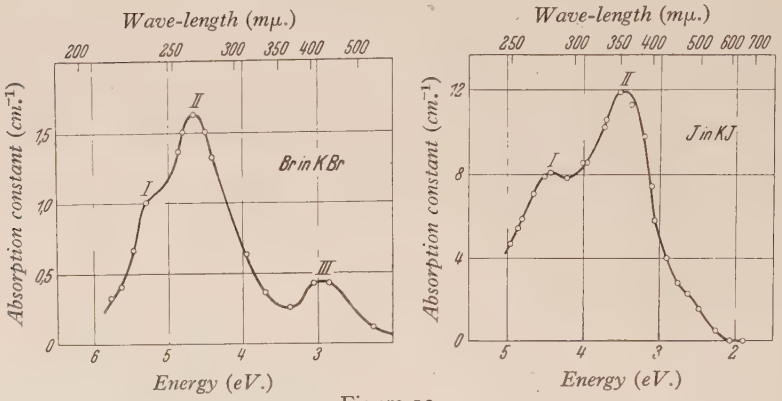


Figure 13.

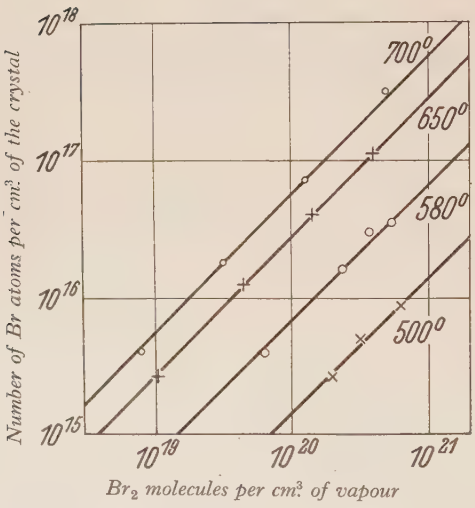


Figure 14. Solubility of Br in a KBr crystal.

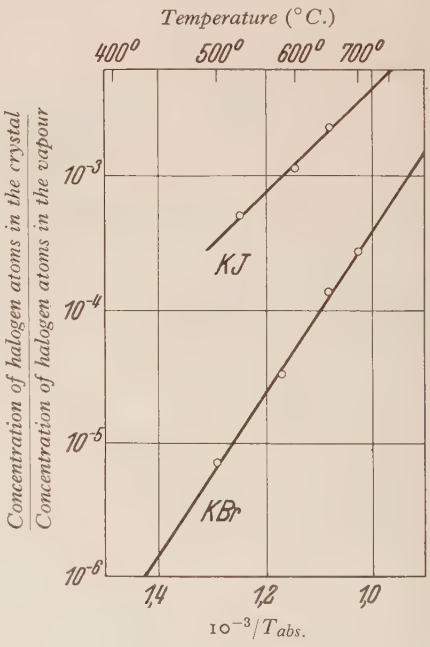


Figure 15.

never reaches unity. Furthermore, it decreases with decreasing temperature of the crystal (see figure 15). The process may here again be treated formally as a solution

and a binding-energy of the halogen calculated, just as was done in the case of the excess alkali. This time the binding-energy is negative, being

$$w_{Br} = 1{\cdot}2 \text{ eV. for KBr}$$

$$w_J = 0{\cdot}8 \text{ eV. for KJ.}$$

This amount of energy must be given to the crystal in order to introduce an excess halogen atom[83], forming a molecule (see below).

The crystals, coloured at high temperatures, must be quickly quenched to room-temperature. Otherwise the excess halogen separates in individual clots as foreign bodies similar to the formation of colloidal metal particles. The maximum in the absorption spectrum of KBr, designated as III in figure 13, is due to such a precipitation, a slight amount of which is practically unavoidable.

The absorption spectra, i.e. the double bands I and II in figure 13, can thus by no means be ascribed to free halogen atoms. Rather similarly to the spectra of the Farbzentren, they are due to an adsorption compound of the type of KJ_3. The similarity between the absorption spectra of figure 13 and those obtained by de Boer and Custers[89] for the adsorption of halogen on vacuum-sublimated CaF_2 films speaks convincingly for this interpretation.

The mechanism of diffusion, by which the halogen penetrates into the crystal, is quite interesting. The discussion of this, as well as diffusion in the case of the formation of the Farbzentren will be dealt with in connexion with that of conduction (§§ 8 and 9).

PART 2. PHOTOELECTRIC CURRENTS IN THE CRYSTALS

§7. PHOTOELECTRIC PRIMARY CURRENTS IN CRYSTALS WITH EXCESS METAL ATOMS (FARBZENTREN)

The migration of the electrons ejected by the light and their replacement are designated as primary* photoelectric current. This replacement is necessary in order to neutralize the excess positive charge left on the atoms after the migration of electrons, and this can take place in two ways. In the first place, electrons which are later on ejected between the positively charged atoms and the cathode by thermal motion or by light ("electron-replacement-conductivity") may move in. Secondly, the neutralization may result due to electrolytic conductivity of the basic material[47]. Unneutralized charges give rise to a polarization and decrease the electric field, often reducing the stationary photoelectric currents to values far below their initial values. This error can always be avoided by going over to the limiting case of sufficiently small light intensities. The fulfilment of this experimental condition is imperative.

* In contrast to photoelectric secondary current. This is lacking in the alkali-halide crystals, but in former years caused difficulties in the investigation of photoelectric properties in other crystals. The secondary currents are released in relay-fashion by the light, whereby an electron conductivity (already present without the presence of light) is increased for a long time by the action of the light. The numbers of electrons constituting the secondary current may exceed by a large factor those released by the light by a large factor. Compare the work of W. Lehfeldt[90].

The course of the primary photoelectric current as a function of time is strongly dependent upon the temperature[1,70]. Figure 16 shows this for the case of a NaCl crystal containing Farbzentren[72].

The total time of observation is divided into three intervals *A*, *B* and *C*. During the interval *A*, light is absorbed in the Farbzentren; *B* is an interval of darkness; and during the interval *C* the crystal is irradiated by light of long wave-length, which is absorbed practically solely by the *F'* centres.

At low temperatures, during the light-absorption in the Farbzentren there appears a practically constant current i_e, without any time lag[5]. This is interpreted as

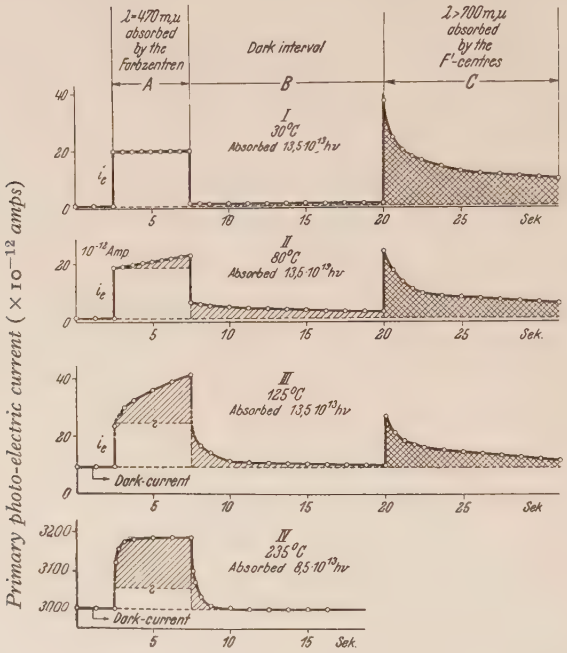


Figure 16. NaCl crystal with $8 \cdot 10^{15}$ Farbzentren per cm³. Distance of electrodes = 4,2 mm.; $E = 1{,}07 \cdot 10^5$ V./m.

follows[1,48]: the electrons ejected from the Farbzentren move towards the anode, and after traversing a mean range (*Schubweg*) *w* are brought to rest. This range is composed of many mean free paths and is usually much smaller than the distance *d* between the electrodes. Furthermore, exhaustive measurements have shown that it is proportional to the electric field strength *E*. The range is that component of the paths of the electrons in the direction of the anode in which their number is decreased to $1/e$ of the initial number, i.e. to 37 per cent. At the end of their range the electrons by combination with positive ions in the lattice form new centres with looser binding, which are *F'* centres.

At higher temperatures there appears during the period of illumination and after it during the dark period a decaying current whose course is shown by the shaded portion of the current-time curve. The interpretation of this is as follows:

The distance between the electron and the positively charged atoms is increased by thermal motion in the electric field. The electrons loosely bound in F' centres are dissociated thermally, proceed in the electric field, and are then again recaptured. This process can occur repeatedly, until the electron is again captured in an F' binding. Finally at low temperatures the thermal action can be either replaced (section I) or augmented (sections II and III) by a light-absorption in the F' centres as shown by the cross-hatched current-time areas of figure 16[1,12].

In making quantitative observations, either the initial lagless primary photoelectric current i_e is measured, or, at higher temperatures, the total current-time area, including the non-shaded parts in figure 16. The relations which hold for this case are:

$$\eta \frac{w}{E} = \frac{i_e}{J_{\text{abs.}}} \frac{d}{E} P \qquad \text{.....(10),}$$

and

$$\eta \frac{w}{E} = \frac{idt}{E_{\text{abs.}}} \frac{d}{E} P \qquad \text{.....(11).}$$

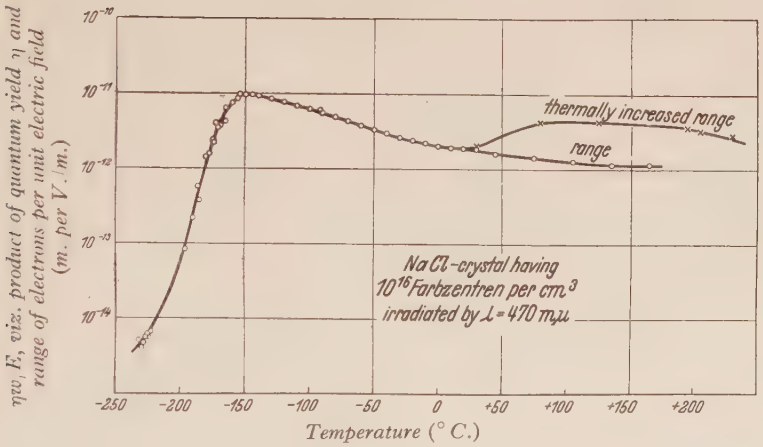


Figure 17.

In these equations, η is the as yet unknown quantum-yield (i.e. ratio of electrons set free to number of quanta absorbed), E the field-strength in Volt/m., d is the distance between electrodes, in m., $J_{\text{abs.}}$ the energy per sec. of the absorbed light, measured in watts, $E_{\text{abs.}}$ the energy of the absorbed light, measured in watt. sec., $P = h\nu/e$, measured in volts ($e = 1{,}6 \cdot 10^{-19}$ amp. sec.), and h is Planck's constant $6{,}55 \cdot 10^{-34}$ watt. sec^2.

The measurements were carried out at different temperatures, but without the introduction of long-wave-length light such as would be absorbed by the F' centres. This corresponds to the time intervals A and B in figure 16. Figure 17 shows the results for NaCl. For temperatures below 30° C. the course of the photoelectric current as a function of time corresponds to I of figure 16; for temperatures above 30° C., however, it corresponds to II–IV. Below 30° C. the electron ranges are calculated according to equation (10), and above 30° C. according to both

equations (10) and (11) wherever possible, and at the highest temperatures by means of equation (11) alone. In this way one finds, for temperatures above 30° C., both the initial range (circles) and the additional thermally increased range (crosses). Both have been reduced to unit field-strength (1 V./m.) and multiplied with the as yet undetermined quantum-yield η.

Corresponding measurements have been made for NaBr, KCl, KBr, KJ, RbCl, RbBr and RbJ. In all cases essentially the same relations are found to hold. As a second example, figure 18 shows the measurements for KCl[85]. The types of currents appearing at different temperatures have been schematically represented in the first row. Figure 18 shows a secondary effect not present in figure 17, namely a further increase in the range at the lowest temperatures.

A discussion of figures 17 and 18 should for the time being be limited to the first rise of the curve labelled "range", i.e. down to −150° C. for NaCl and to

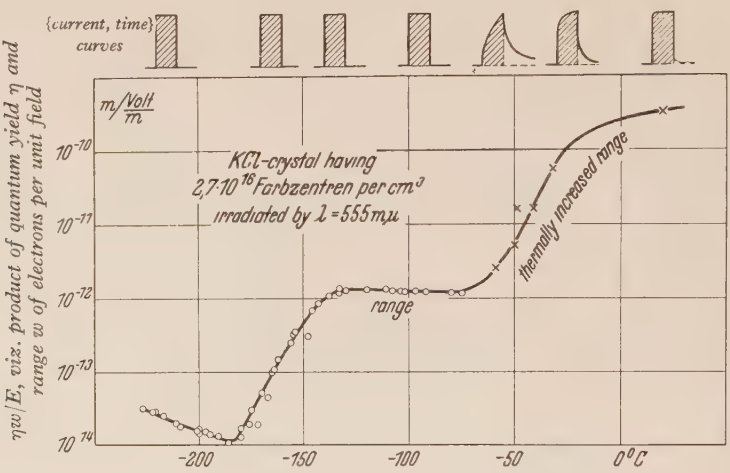


Figure 18.

−130° C. for KCl. If a light quantum is absorbed in this temperature interval, not only a Farbzentrum disappears, but there is also produced an F' centre (§ 5). Therefore it is allowable to put $\eta = 1$ in equation (10) and (11), i.e. to assume an electron is liberated from a Farbzentrum for each light quantum absorbed, and is again fixed in an F' binding. In this case the curves through the circled observed points may be taken directly as the ratio

$$\frac{w}{E} = \frac{\text{range of electrons}}{\text{field-strength}}.$$

The ratio w/E is proportional to a specific electric conductivity[77, 81]. This increases initially with decreasing temperature not only for metals but also for isolating crystals as well. The absolute value of the temperature-coefficient is also of the same order of magnitude as for metals. Below the temperature designated, the value of η is as yet unknown. It is not known whether the sharp decrease of the measured value of $\eta\, w/E$ is due to a decrease of η or of w/E. A decrease of the

mean range w would occur if some of the electrons liberated by light drop back into the metastable F' level of the same atom, instead of forming a new atom with a *distant* cation and taking a place in its F' level.

The new rise of $\eta\, w/E$ below $-180°$ C. in KCl is certainly due to electrons which are liberated not from Farbzentren but from traces of colloids. Their small effect is not noticeable at high temperatures.

A further fact is important for the interpretation of this electron movement. The range of the electrons per unit field strength w/E is inversely proportional to the concentration of Farbzentren throughout a wide range of concentrations (figure 19). The measurements are for KCl at $-100°$ C. and these have been made upon five different crystals, in order to show the magnitude of the individual variations[85].

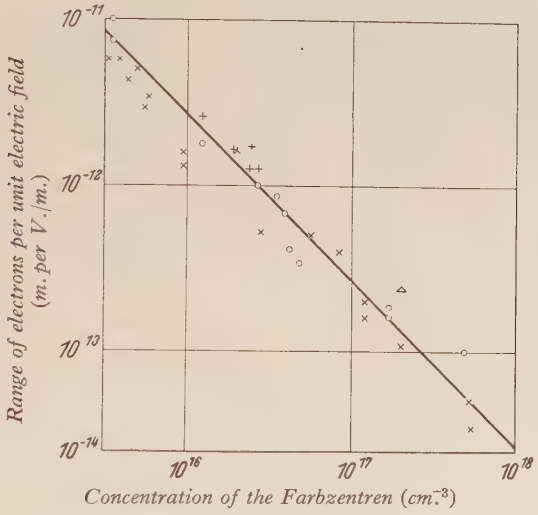


Figure 19. KCl at $-100°$C.

$1/w$ has the significance of an absorption-constant K_e as in equation (1), if $\mathfrak{J}_e$ denotes the initial number of electrons and $\mathfrak{J}_d$ their number after having moved a distance d towards the anode (this presupposes that the zig-zag path of the free electrons is large compared with the mean distance between Farbzentren). $K_e = 1/w$ is proportional to the concentration of Farbzentren, according to figure 19. Accordingly, the absorbing cross-section due to *one* Farbzentrum in the crystal may be calculated by means of equation (3) and at $E = 1$ V./m. this turns out to be $\beta_e = 4 \cdot 10^{-11}$ m^2 for KCl, with numbers at the same order of magnitude for NaCl, KBr, RbCl, and RbBr.

Up to this point only the curves designated as "ranges" (circles in figures 17 and 18) have been considered. At higher temperatures the thermally increased ranges (denoted by crosses) have also been drawn. These are produced by a thermal diffusion of the F' centres. This diffusion is concluded only when all the electrons have returned to the stable Farbzentren binding. The paths traversed by the electrons up to this point in the case of KCl exceed the original range by up

to 500-fold. At $+20°$ the value of w/E is $5 \cdot 10^{-10}$ V./m. At a field-strength of 10^6 V./m. the total path traversed by the electrons is thus 0·5 mm. In this case the electrons released by light in a crystal plate a few tenths of a mm. thick can be entirely withdrawn by the electric field and the primary photoelectric current then becomes saturated[17,31].

Note added in proof. In favour of the hypotheses that the fall in $\eta w/E$ at low temperatures shown in figures 17 and 18 is due to a fall in η, we must add the fact that the quantum yield of the optical transition also decreases, and thus, apparently more than in proportion, the number of electrons which can move through the lattice decreases too. The drop in temperature inhibits the source of electrons, not the mechanism of conduction.

In favour of this explanation we may mention the observations made with KCl at low temperatures (figure 18) of a current due to electrons liberated from colloids by the ordinary surface photoelectric effect, which is known to be practically independent of temperature.

PART 3. MOTION OF ELECTRONS THERMALLY RELEASED

§8. THERMALLY RELEASED ELECTRON CURRENTS IN CRYSTALS HAVING AN EXCESS OF ALKALI METAL

The measurements shown in figures 17 and 18 cannot be carried out at temperatures above approximately 200°, because at higher temperatures not only the F' centres, but the Farbzentren as well are dissociated thermally. Consequently great numbers of free electrons are present even without illumination, in comparison with which the number that can be ejected by light is negligible.* For this reason Farbzentren cannot be used at high temperatures for the releasing of electrons by optical means. The thermal dissociation affects not only the Farbzentren, but also the lattice of the crystal, and thus the electrolytic conductivity of the basic material reaches a considerable value. At this stage, this electrolytic conductivity is able to neutralize the positive residual charges caused by the migration of great numbers of electrons.

At high temperatures these two facts cause the Farbzentren to migrate towards the anode as a swarm[33] (figure 20). This migration takes place with a definite rear wall. While the eye follows this, a current-measuring instrument shows the current-time curve[33] shown in figure 21.

Figure 20 corresponds formally to a series arrangement of two crystals having different electrical conductivities. In the part which is already clear, only ions migrate, whereas both ions and electrons migrate in the part still filled with Farbzentren. The number N of Farbzentren originally present in the crystal, which have

*. Using monochromatic light, more than some 10^{14} quanta per sec. per cm^2 can hardly be introduced.

migrated out of it due to the electric field can be calculated from the shaded current-time area, $\int idt$ of figure 21. Here

$$N = 2\frac{\int idt}{e} \qquad \text{.....(12)}$$

where $e = 1{,}6 \cdot 10^{-19}$ amp.sec. assuming that the electrolytic conductivity in the coloured part is no greater than in the clear part, in spite of the presence of the

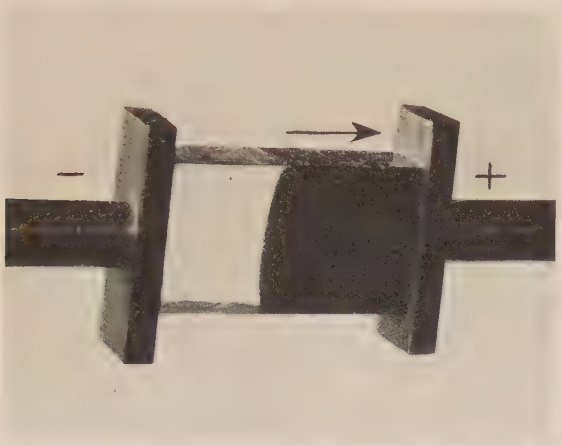


Figure 20.

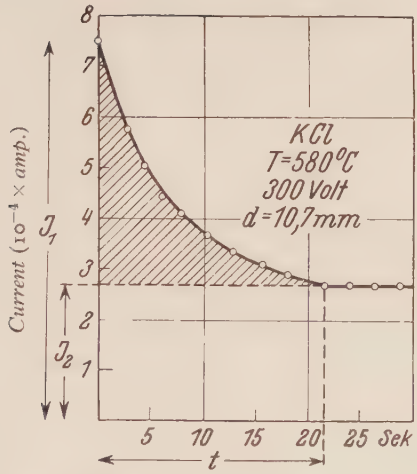


Figure 21. Electric current during the migration of Farbzentren.

Farbzentren. Otherwise the factor 2 in equation (12) must be replaced by a smaller value, between 2 and 1 [51].

The experiment represented in figure 20 can be varied. For example, electrons may be made to enter the crystal from a pointed cathode [36]. A flat and previously anodically polarized cathode can also be used. In this way the whole crystal can be

homogeneously filled with a Farbzentren swarm and an electron current i, constant with time, is obtained. The ionic current i_i due to the non-coloured crystal is superposed upon this. The relevant equation is

$$i = N_0 F e v_f \frac{P}{d}$$

where N_0 is the number of Farbzentren per cm^3, F the cross-section of the crystal, $e = 1{,}6 \cdot 10^{-19}$ amp.sec., d is the distance between electrodes in m, P the applied voltage and v_f the mobility of Farbzentren in m.-sec.$^{-1}$/V.-m.$^{-1}$

The visible migration of the electron swarm is easily interpreted. The thermal dissociation of the Farbzentren produces invisible alkali-metal ions and electrons. The electrons are able to diffuse very quickly in the crystal lattice in traversing their free paths between the atoms of the lattice. If an electric field is applied to the crystal, the diffusion receives a preferential direction towards the anode. In this free condition each electron has only a limited life. This ends when the electron is captured by a positive ion and becomes fixed in the formation of a Farbzentrum. The electron then remains in this condition for some time, until it is again ejected by thermal motion, and the whole process starts over again. Only during these rest periods during which the electron is bound in the Farbzentrum, is the location of the electron rendered visible and in this way the path of the electrons towards the anode can be followed. Apparently, visible Farbzentren, i.e. neutral metal atoms, migrate; in reality, however, the migration is that of invisible electrons[67, 71].

The mobility of the Farbzentren, i.e. their speed of migration in unit electric field, can be measured in different ways. The simplest way is to observe a small, definitely bounded Farbzentren swarm in an otherwise clear crystal and to measure the velocity directly with a scale and stop-watch[44]. Equation (12) may also be used[50] or measurements such as those represented in figure 20 may be applied. The equation here applicable is[51]

$$v_f = \frac{1 + \frac{1}{2}(J_1 - J_2)/J_2}{TP} d^2 \qquad \ldots\ldots(13)$$

(compare figure 10). Here T is the absolute temperature, P the applied voltage and d the distance between the electrodes.

The mobility measured in this way increases with the temperature of the crystal. Figure 22 shows this for nine salts. In all cases the mobility increases exponentially with temperature[44], according to the empirical formula

$$v_T = v_0 \, e^{-w/kT} \qquad \ldots\ldots(14)$$

where $e = 1{,}37 \cdot 10^{-23}$ watt-sec./degree and w is a work-function.

Interpretation: with increasing temperature the thermal dissociation of the Farbzentren into ions and electrons increases, or, expressed in another way, the rest-periods of the electrons during their binding in the Farbzentren become shorter. In the limiting case of high temperatures these rest-periods disappear entirely and the mobility of the Farbzentren reaches its limiting value v_0. Several values[50] of v_0 will be found in table 2. These values are taken from the measurements represented in figure 22 and are not claimed to be exact. The limiting

mobilities v_0 are of the same order of magnitude as that of the electrons in copper and in other metals of high conductivity.

Table 2.

	NaCl	NaBr	NaJ	KCl	KBr	KJ	RbCl	RbBr	RbJ
Limiting mobility v_0 m.-sec.$^{-1}$/V.-m.$^{-1}$	0·002	0·066	0·074	0·014	0·017	0·020	0·011	0·013	0·014
Thermal work function (eV.)	0·94	0·80	(0·76)	1·00	0·84	0·83	0·84	0·68	0·63

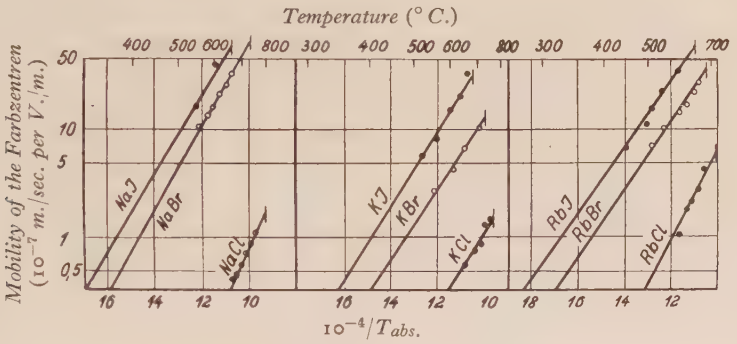


Figure 22. Mobility of Farbzentren.

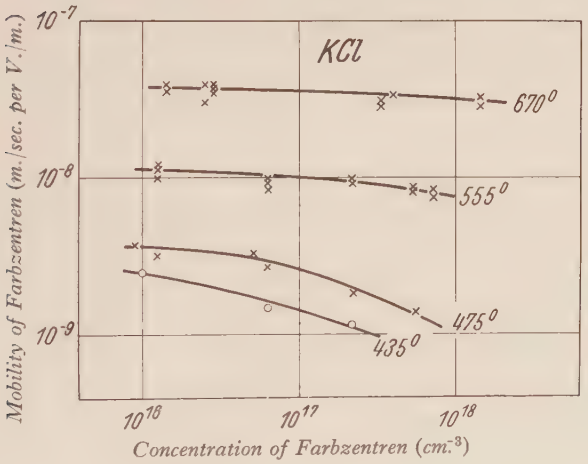


Figure 23.

In the experiments thus far discussed, small concentrations of Farbzentren have to be used. Otherwise the case might occur in which the electrolytic conductivity is not sufficient to neutralize the positive residual charges and thus the measured mobility is too small. Actually the concentration affects the true mobility, but its influence is very small, as figure 23 shows. It is only noticeable at low temperatures,

the mobility of Farbzentren being practically constant at high temperatures [80] up to concentrations of $10^{18}/cm^3$.

By a proper choice of temperature-scales the curves of figure 23 for salts having the same cation may be made to coincide. In figure 24 the abscissae give the absolute temperature divided by a characteristic temperature for each salt, similar to that which may be derived from the specific heat as a function of the temperature, or in other ways. The ordinates, i.e. the mobilities of the Farbzentren, in contrast to figure 23, are plotted linearly, not logarithmically. From this it seems clear that the degree of dissociation of the Farbzentren, i.e. the exponential factor in equation (14), is determined practically by the thermal motion of the lattice.

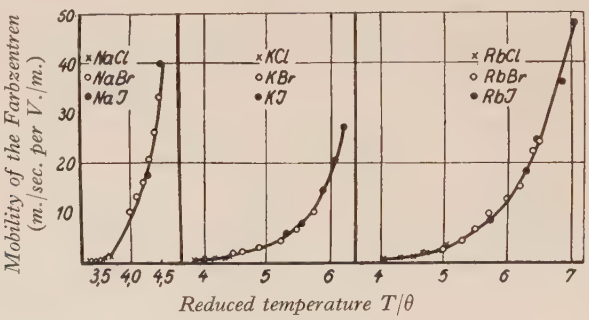


Figure 24.

If no electric field is applied to the crystal, the electrons which are thermally ejected diffuse in all directions [65]. The diffusion-constant D can be measured and the same connexion between it and the mobility exists here as for these quantities in the case of ions in solutions [74]. In the limiting case of high temperature or of very small concentrations the following simple relation is found to hold:

$$v_F = D\frac{e}{kT} \qquad \ldots\ldots(15),$$

where v is in m.-sec.$^{-1}/V$.-m.$^{-1}$ and D in m.^{2}/sec., $k = 1{,}37 \cdot 10^{-23}$ watt-sec./degree, and T and e are as in equation (14).

Beyond these limiting cases, the electrolytic conductivity of the basic material and the mechanism of ionic conduction must be considered [65, 56, 57].

The thermal diffusion of electrons also explains the phenomenon described in § 3, namely the production of Farbzentren by heating the crystal in the presence of the cation metal.*

§ 9. THERMALLY RELEASED ELECTRON CURRENTS IN CRYSTALS WITH EXCESS HALOGEN

The process discussed in § 8 may be concisely described as electron-excess conductivity. Neutral alkali atoms (Farbzentren) are changed over into positive ions, i.e. normal lattice elements, by giving off excess electrons. The counterpart of

* J. Eggert and W. Noddack [91] first introduced the idea of tracing back metallic diffusion to the diffusion of electrons, in order to explain the flocking together of silver atoms in AgBr crystals.

this, an electron-deficiency conductivity, can be observed in crystals having a stoichiometric excess of halogen atoms.* Here the visible neutral halogen is changed back into a negative ion, i.e. a normal lattice element, by taking up a lacking electron. This may take place in an electric field, according to the mechanism of electron-replacement (§ 7), if the thermal motion makes a thermal diffusion of electrons possible. Then a neutral halogen atom abstracts an electron from one of its neighbours between it and the cathode, and thereby itself becomes an invisible ion. At the same time it transforms its neighbour into a visible halogen atom. In this way the visible swarm of excess halogen wanders towards the cathode[61]. The process is exactly the same as that illustrated in figure 20, with changed sign of the electrodes. Here again apparently a neutral halogen migrates in the electric field. Actually, however, electrons migrate according to the scheme of a replacement current.

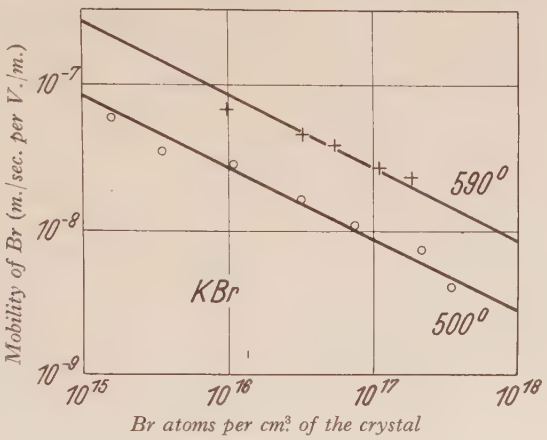


Figure 25.

Everything explained in § 8 may accordingly be applied to the electric measurements on crystals with excess halogen. Thus, for example, the current-time relation for the migration of a halogen swarm has the same form as in figure 21. The number of halogen atoms can be determined by equation (12). Furthermore the mobility of the halogen can be measured in exactly the same way as in the case of Farbzentren. In contrast with the Farbzentren, however, the halogen-mobility is greatly affected by the concentration[83], as shown by figure 25. Here also, however, the mobility increases with increasing temperature of the crystal, as figure 26 shows[83]. The relation between the mobility v_T and the temperature may again be represented by the empirical equation (14). Table 3 contains several values for the limiting mobility v_0 and the work function w.

Thus there is an extensive analogy between electron-excess conductivity and electron-deficiency conductivity. However, there are noticeable quantitative dif-

* The meaning of a stoichiometric excess of electron-negative lattice-element for thermally released electron currents was, to my knowledge, first recognized by B. Gudden[92]. From this C. Wagner and W. Schottky have made deductions which are important in the problem of semiconductors.

ferences. These pertain particularly to the thermal diffusion of halogen without application of an electric field. This difference was utilized in § 6 in the production

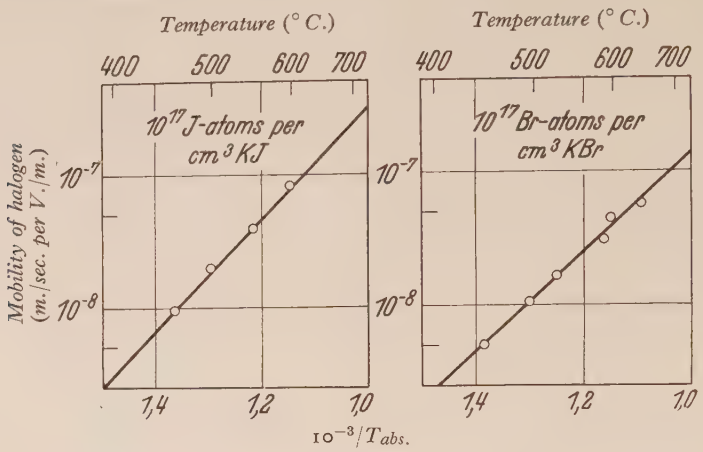


Figure 26.

Table 3.

	KBr	KJ
Limiting mobility v_0 (m.-sec.$^{-1}$/V.-m.$^{-1}$)	0,0007	0,005
Thermal work function (eV.)	0,7	0,8

of a stoichiometric halogen excess. This process takes place only partially by electron-diffusion. In the case of KBr under a halogen pressure of one atmosphere, for example, about 50 per cent of the diffusing molecules do so as uncharged bromine molecules[83].

PART 4. PHOTOCHEMICAL PROCESSES

§ 10. INTRODUCTION

The investigations of photochemical processes in solid bodies are carried out almost solely upon the silver salts, especially AgBr. This emphasis upon the silver salts is due to the extraordinary importance of photography. The majority of the investigations employ the conditions of exposure usual in photographic practice. Approximately 10^{14} light quanta per cm³ are absorbed, and the number of molecules transformed, or the number of individual nuclei produced from them, is of the same order of magnitude. Under these conditions the action of the light is latent, since the silver-salt film of the photographic plates, etc. has a thickness of only a few μ. and consequently there are but 10^{10} transformed molecules under each cm² of surface[24, 38]. In thicknesses as small as this, new molecules can first be optically observed when their concentration reaches 10^{18}/cm³, or when there are at least 10^{14} transformed

molecules under each cm^2 of surface. For this reason, the aid of chemical development is necessary for investigations of such thin photographic films. A number of atoms of silver many thousands of times larger than the number of molecules originally transformed by the light must be deposited upon the primary reaction-products (or the nuclei resulting from them). If one wants to work without development, for example, with printing-out paper, at least 10^{18} quanta per cm^3 must be absorbed, a number far different from the normal-exposure condition.

Chemical development, although its practical use is very great, introduces serious difficulties into the investigations of photochemical questions. For this reason it seemed very interesting to be able to avoid the use of chemical development in the investigations of photochemical processes in solid bodies, and to make the elementary or latent action of the light directly observable. This problem was solved in a very simple manner for alkali-halide salts. The primary photochemical reaction-products in these are the Farbzentren. It is easy to work with clear crystals of 1 cm. thickness or more. It is sufficient, as in normal photographic exposure, to absorb approximately 10^{14} light quanta per cm^3. This results in 10^{14} Farbzentren under each cm^2 of surface, whereas in the thin photographic films the corresponding number was but 10^{10}. These 10^{14} Farbzentren are capable of investigation both optically and electrically. In this way it is possible to perform experiments upon the latent action of light, whose results may accordingly be applied to the technically important silver salts[26].

§ 11. PHOTOCHEMICALLY ACTIVE LIGHT-ABSORPTION

For the silver salts used in photography, the active spectral range coincides with the absorption band of AgBr extending into the visible. For many years the elementary process in photography has been interpreted as a removal of an electron from a halogen ion to a metal cation. The primary reaction-products were thought to be neutral silver atoms, and these were to be the preliminary step in the formation of the development-nuclei. In line with these photographic investigations, we at first used light, which was absorbed in the region of the first ultra-violet band of the crystal (figures 4 and 5) also in the case of alkali salts[25]. This choice was favoured by the fact that the frequencies of the first band of all the salts can be satisfactorily calculated by assuming an electron transition from the anion to the cation and utilizing an empirical formula containing, aside from the lattice constants, only the ionizing potential of the metal and the two electron-affinities of the halogen[23, 35]. For experimental reasons, only the long-wave end of the first absorption band could be used, for it was necessary to achieve a homogeneous penetration of photochemically active light through a crystal approximately 1 cm. thick. For the wavelength of the maximum of the first bands a thickness of only 0·01 μ. can be penetrated, because the absorption-constant here has a value of approximately 10^{-6} cm^{-1} (table 1). We may use only 10^{14} quanta per cm^3 in a volume 10^{-6} cm^3, giving 10^8 centres below an area of 1 cm^2, a much less favourable case than the 10^{10} per cm^2 in photographic plate.

This choice of photochemically active wave-length was, however, exceedingly unfavourable in another respect. The light-absorption in the long wave-length end of the first absorption band can, as stated above, be due to molecules of the lattice, which are thermally or otherwise disturbed and hence will respond to low frequencies. No less probable, however, is the absorption of light by foreign molecules[46], which can cause absorptions of the amount here utilized even when present only as impurities in a ratio of $1 : 10^6$. For this reason it was necessary to find a photochemically active light-absorption whose centres were definitely known. This has been possible.

The most favourable conditions exist in alkali-halide crystals containing small amounts of alkali hydride[78]. Such mixed crystals may be produced in a number of ways. The best method is that of heating a crystal containing Farbzentren in an atmosphere of H_2. The H_2 diffuses rapidly into the crystal and changes the visible Farbzentren into invisible hydride molecules. At a pressure of 100 atmospheres this diffusion takes place with surprising speed, at a rate of approximately 1 mm./sec. (This is a diffusion of molecules, not protons[84]!) The alkali hydride, colourless in visible light, has a bell-shaped absorption band in the ultra-violet. Figure 27 shows the measurements for KH in KBr. These absorption bands were formerly designated as *U* bands of the salt, their origin then being unknown[39].

In a similar way crystals containing K_2O crystals can be produced, and their well-defined light-absorption utilized for photochemical purposes[55, 62]. Certainly the number of usable additions is much greater[69, 76], but systematic investigations are still lacking.

§ 12. MEASUREMENTS OF THE PHOTOCHEMICAL YIELD BY OPTICAL AND ELECTRICAL MEANS

In gases, the photochemical dissociation of molecules is dependent not only upon the absorption of a light-quantum but also upon the thermal vibrational energy of the molecules as well. The same is true for the photochemical processes in the alkali salts, and also the optical dissociation of KH into invisible hydrogen and visible Farbzentren for example[52]. If light is absorbed in the KH band (figure 27), this band disappears, and in its place the band of the Farbzentren appears. Figure 28 shows the yield of this photochemical reaction as a function of the temperature. This may be represented by the equation:

$$\eta_T = 1 - (1 - e^{-\epsilon/kT})^A \qquad \ldots\ldots(16),$$

where $\epsilon = 0{\cdot}85$ eV. and A has a value between 7 and 8[59, 82].

The number of Farbzentren formed was determined optically up to approximately 150° C. At higher temperatures this method fails, because the life of the Farbzentren becomes too short, due to their thermal transformation back into KH molecules[64]. At higher temperatures, accordingly, an electrical method was applied for the measurement of the Farbzentren. The crystal is illuminated by light of known intensity, generally some 10^{-6} watt, amounting to some 10^{12} quanta per second, and the stationary photoelectric current is measured. If this is considerably

smaller than the electrolytic dark current of the crystal, the current voltage curve shows a definite saturation (figure 29). The number of electrons migrating to the anode, and hence the number of Farbzentren formed, can be calculated from the saturation current[59]. At the conclusion of the photochemical irradiation, the

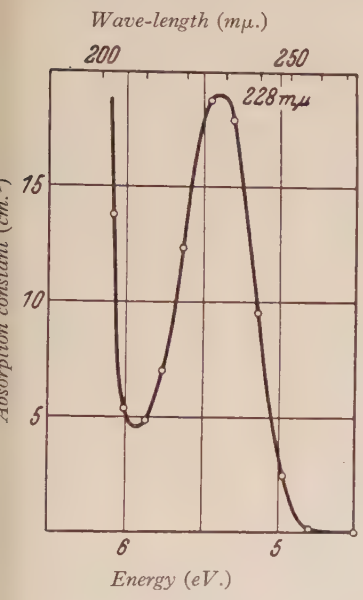


Figure 27. KH in KBr.

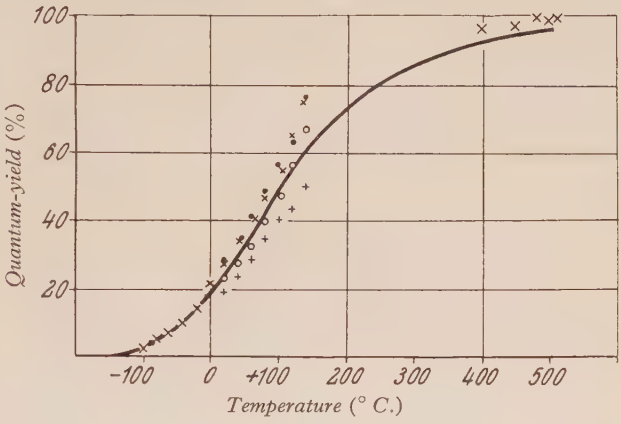


Figure 28.

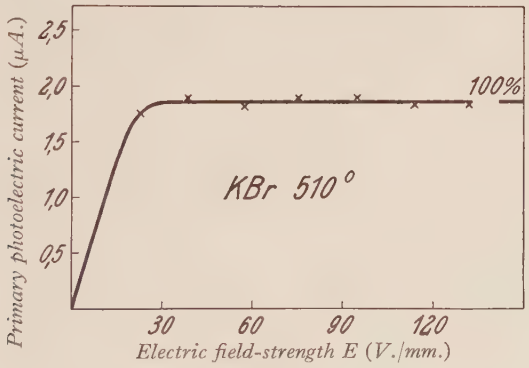


Figure 29.

remainder of the Farbzentren can be observed as they move out of the crystal[46, 63, 73], just as is illustrated in figure 20.

Here the photoelectric current is solely an aid for the measurement of the number of Farbzentren formed, and thus of the quantum-yield. By utilizing electrical and optical measurements simultaneously, further questions, relating to the mechanism of the elementary process, can be investigated. For example, it turns out that the optical dissociation of the KH molecules and the formation of Farb-

zentren is not accompanied by a measurable current. The electron-transfer takes place only in molecular dimensions[76].

Electrical methods for the investigation of the photochemical elementary process may still be used even at low temperatures. If the number of Farbzentren formed in the available thickness of crystal does not suffice for the optical detection of these Farbzentren, the following method may be employed. Light is absorbed in the Farbzentren band, and the electrons can there be made as mobile as in the case discussed in § 7[29].

The investigation of photochemical processes in solid bodies is still in a very early stage. But a few of the facts found have been mentioned here. Still, the above illustrations will have served to show that these processes can be successfully investigated with physical means, i.e. optical and electrical observations, alone.

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TRAPPED ELECTRONS IN POLAR CRYSTALS

By R. W. GURNEY and N. F. MOTT

RECENTLY several attempts have been made to explain the nature and account for the properties of the F centres in terms of the atomic theory of polar lattices[1,2,3,4], and it is a matter of dispute to what extent crystal imperfections and faults are essential for the understanding of this phenomenon. In this paper we shall attempt to show how an extra electron may be expected to behave in a crystal *without* crystal imperfections, if we accept the current theory of polar lattices, and shall then make some tentative suggestions about the connexion between our findings and the experimental material. The paper is based on an idea due originally to Landau[5] and developed further by Frenkel[6] and by ourselves. A very similar idea has been used by von Hippel[2].

If we imagine an extra electron brought from outside and placed on one of the metal ions of an alkali-halide crystal, then we should expect that electron to be free to move from one metal ion to the next through the crystal. Such an electron cannot be spoken of as belonging to any particular metal ion, and we speak of it as being in the conduction level of the crystal as a whole. In a crystal which shows photoconductivity the action of the light is to raise electrons from lower, bound, levels into the conduction level.

Now the dielectric constant of a polar crystal is due partly, as in non-polar materials, to the polarizability of the atoms or ions of which it is built up, and partly to the actual displacement of the positive and negative ions in opposite directions by the applied electric field. Owing to the large mass of the ions, they can only be displaced by alternating fields with frequency less than about 10^{12} sec.$^{-1}$ (the Reststrahlfrequenz).

We have used the methods of wave mechanics to investigate the motion of an electron in the conduction band and find that, as in a metal, an electron will not in general stay in the neighbourhood of any one ion for more than about 10^{-15} sec. The field of the electron itself, therefore, changes too rapidly to be effective in polarizing the medium. But suppose that "by accident" an electron remains on one positive ion for about 10^{-12} sec. Then the medium round about will have time to become polarized, the positive ions being displaced towards and the negative away from the electron as shown in figure 1 *a*. The electrostatic field vector E at a distance r from the electron will decrease (numerically) from $e/\kappa_0 r^2$ to $e/\kappa r^2$, where κ_0 ($\sim 2{\cdot}5$) denotes the dielectric constant due to the polarization of the ions only, and κ (~ 5) is the dielectric constant for static fields due to the polarization *and* to the displacement of the ions. The field due to the polarized medium is thus

$$\left(\frac{1}{\kappa}-\frac{1}{\kappa_0}\right)\frac{e}{r^2} \qquad \ldots\ldots(1).$$

This field will now push the electron back if it tries to escape; the potential energy of an electron in this field is

$$V(r) = -\left(\frac{1}{\kappa_0} - \frac{1}{\kappa}\right)\frac{e^2}{r} \qquad \ldots\ldots(2).$$

A "potential hole" is thus formed by the displaced medium, and in this potential hole the electron will have a series of stationary states, just like the stationary states in the field of a proton, for which $V(r) = -e^2/r$. We shall speak of an electron in the lowest of these states as a "trapped electron".

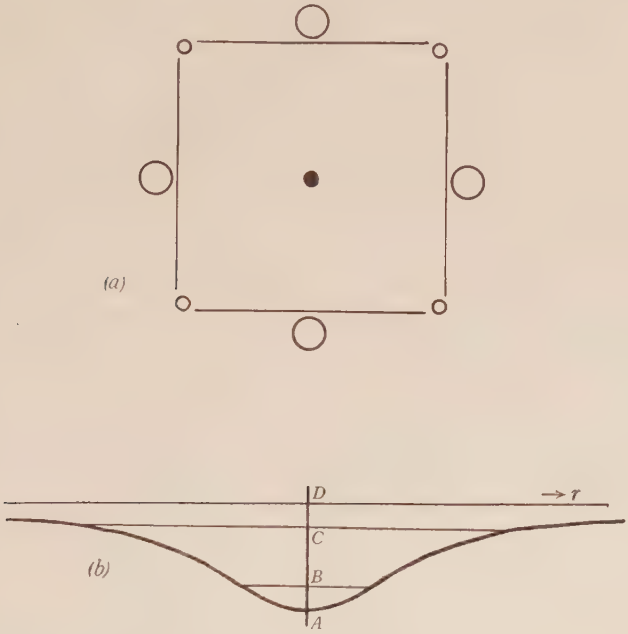

Figure 1. (*a*) Displaced ions round a trapped electron. (*b*) Potential energy of an electron in polarized crystal; the horizontal lines at *B* and *C* represent the energies of the normal and excited states. ● positive ion with electron; ○ positive ion; ◯ negative ion.

An electron trapped in this way can only move from one ion (*a*) to a neighbouring ion (*b*), if *at the same time* the surrounding ions move into new displaced positions about the ion (*b*). The frequency with which such a process takes place may be shown to be very small at room temperature[6], so that we may assume that our trapped electrons are immobile. At high temperatures, however, thermal vibrations may occasionally raise an electron from its trapped position into the conduction band.

Formulae (1) and (2) are valid only at large distances from the electron such that $r \gg a$, where a is the nearest distance between unlike ions. This is for two reasons: first, these formulae neglect the atomic structure of the crystal, and will be entirely incorrect when $r < a$; and secondly, an electron trapped in our "potential box" will have an orbit (wave function) of finite radius comparable with a, and some of the

nearest ions will be acted on by a field due to *less* than one electronic charge. The potential energy of an electron in the field due to the displaced ions may be expected to appear as in figure 1 *b*. In this figure *B* and *C* represent normal and excited states.

We have estimated the depth of the potential hole *AD* in figure 1 *b* in a way which will be clearest if we neglect for the moment the polarizability of the ions and so set $\kappa_0 = 1$. Then at large distances the polarization of the medium is

$$P = \frac{1}{4\pi}\left(1 - \frac{1}{\kappa}\right)\frac{e}{r^2},$$

and thus the displacements of the ions are

$$x = \pm \frac{1}{4\pi}\left(1 - \frac{1}{\kappa}\right)\frac{a^3}{r^2} \qquad \ldots\ldots(3).$$

If we were to assume formula (3) to be valid for *all* the ions of the lattice, we should obtain for the potential at the centre

$$-\frac{e^2}{4\pi}\left(1 - \frac{1}{\kappa}\right)\Sigma\frac{a^3}{r^4} = 1{\cdot}31\left(1 - \frac{1}{\kappa}\right)e^2,$$

where the summation Σ over the distances from a given ion to all the other ions of a simple cubic lattice was carried out using formulae due to Lennard-Jones and Ingham [7].

What we actually did was to assume equation (3) to be valid except for the six negative ions which are nearest neighbours to the positive ion on which the electron considered is located. We then determined the displacements x of these ions in the field of the electron and the induced dipoles of all the other ions, the latter being summed numerically. A few calculations for the ions distant $\sqrt{2}a$, $\sqrt{3}a$ and $2a$ showed this to be quite a good approximation.

By these methods we found the depth of the potential hole to be from 6 to 4 eV. for the fluorides and from 2·5 to 1·5 eV. for the other alkali halides. The displacement x of the ions which are nearest neighbours is of the order $\frac{1}{10}a$.

In a potential hole of the form shown in figure 1 *b*, an electron will have an infinite series of stationary states just as in a hydrogen atom. We therefore expect a strong-line absorption corresponding to a transition to the first p state, and possibly other weak lines. All lines will be broadened by the vibration of the ions. There will be also a weak continuous spectrum for higher frequencies.

The question now arises, can these trapped electrons be identified with the *F* centres? Both Smekal [3] and de Boer [1] have given quite different explanations. We see that the absorption to be expected is in the same part of the spectrum as the *F* band. We have, moreover, estimated the broadening to be expected as the temperature is raised and find it also in satisfactory agreement with experiment. The photoconductivity observed can be pictured in the following way: the electron is raised by the light to an excited state (*C* in figure 1 *b*), and the thermal vibrations are then sufficient to raise the electron into the conduction band. This will account for the very marked diminution in the current per absorbed quantum observed by Gläser

and Lehfeldt[8] below $-150°$ C.*; the thermal vibrations are *not* then sufficient to remove the electron.

Before, however, we can say with any confidence whether our trapped electrons are F centres, it will be necessary to discuss in the light of the model the various processes by which F centres may be formed, and what happens to the corresponding positive charge. We feel, however, that the theoretical grounds for believing in the existence of trapped electrons are strong, and that it will be surprising if they do not correspond to something in the observed phenomena.

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* Cf. the paper in this volume by R. W. Pohl, figures 17 and 18, pp. 17, 18.

DISCUSSION OF THE PAPERS BY POHL, AND BY GURNEY AND MOTT

Reported by N. F. MOTT

THE discussion was opened by Dr de Boer, who remarked that although Prof. Pohl refused at this stage to advance any hypotheses as to the nature of the F centres (*Farbzentren*) until the experimental evidence should be sufficient to decide unequivocally between them, it was necessary for other people to do so, because of the great importance of this work of the Göttingen school for the understanding of other phenomena. He then proposed a number of alternative models for the F centres, which have already been published (reference 1 of the preceding paper). The following account describes the hypothesis, which, at the end of an afternoon's discussion, appeared the most probable.

It must first be stated that Landau's trapped electrons, described by Gurney and Mott, certainly do *not* correspond to the observed F centres. This follows from the fact (cf. Pohl's article, figure 6) that when a halide crystal is heated in the vapour of the alkali metal, the number of F centres formed is proportional to the pressure of the alkali vapour. If the alkali atom dissociated into a trapped electron and a positive ion (adsorbed perhaps at an internal crack), the number of F centres would be proportional to the square root of the temperature. Whether Landau's trapped electrons correspond to anything in the observed phenomena must remain an open question.

Any explanation based on cracks or defects of an *irregular* nature was ruled out, since Prof. Pohl stated that the spectrum of the F centres was always the same. This was not however definitely established to be the case for the F' centres.

The most probable hypothesis seems to be the following: in an alkali-halide crystal *in thermal equilibrium* at a temperature T one may suppose that at a certain number of positive lattice points, and at an equal number of negative lattice points, an ion is missing (cf. figure 1). The number of such vacant places will be proportional to a factor $e^{-\frac{1}{2}E/kT}$, where

$$E = E_1 + E_2 - E_3,$$

E_1, E_2 being the work required to remove a positive and negative ion respectively and E_3 the lattice energy per ion pair.*

It is now suggested that an F centre is an electron trapped in the neighbourhood of a point where a negative ion is missing. An F centre is thus as a whole electrically neutral.

* A preliminary calculation carried out in Bristol on the basis of the Born lattice theory with polarizable ions gives 1·4 eV. for $\frac{1}{2}E$ in NaCl.

If we neglect the finite radius of the orbit (wave function) of an electron, the energy of an electron located on a positive ion far from any hole will be

$$\frac{\alpha e^2}{r_0} - I \simeq +3 \text{ eV}.$$

where α is the Madelung constant (1·74), r_0 the interatomic distance, and I the ionization potential of the alkali atom. On one of the ions Q next to the missing negative ion the potential is

$$\frac{(\alpha - 1)\, e^2}{r_0} - I,$$

which is about 5 eV. lower, and at the lattice point of the missing ion the energy is $-\alpha e^2/r_0$, which is much lower still, so there is no doubt that an electron could be trapped in such a neighbourhood.*

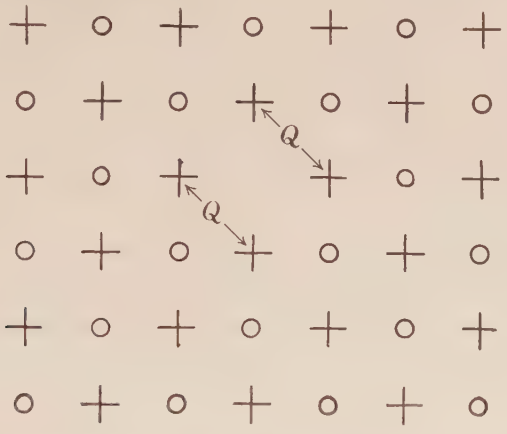

Figure 1. Alkali-halide crystal with one negative ion missing; the crosses represent positive and the circles negative ions. It is suggested that if an electron is trapped in the place left by the negative ion, an F centre is formed.

Dr Verwey suggested that the electron would be trapped on a particular one of the 6 ions Q, and described some recent experiments of his own on the dielectric loss for frequencies of about 200 metres in halide crystals with and without F centres. In the crystal with F centres the dielectric loss was some 50 times greater, although both crystals were insulators for steady fields. Dr Verwey suggested that this loss of energy was due to the electron jumping from one atom Q to another. In subsequent discussion with the present writer, however, it was agreed that the position of lowest energy is the central point, and that in any case an electron trapped in such a potential hole would have a non-degenerate wave function extending over the whole neighbourhood of the six points Q; so the explanation of Dr Verwey's experiments must be found in some other way.

The model given above of the F centres obviously accounts for the dependence of the concentration on the pressure of alkali vapour. Also, when F centres are

* These energies, being calculated neglecting the polarizability of the ions, are probably much too large, but their relative magnitudes are correct.

introduced from a cathode into a hot crystal, halogen is ejected which, according to Prof. Pohl, can be detected by its smell. Further, the explanation of the drop in photoconductive current at low temperatures (Pohl, figure 17) given by Gurney and Mott can be applied to this model also. It also enables one to form a picture of the photochemical transformation of U centres into F centres. Assuming that a U centre is an H^- ion replacing a halogen negative ion in the lattice, the absorption of a quantum in the U band (Pohl, figure 27) will remove an electron on to a neighbouring positive ion, leaving behind a hydrogen atom. At sufficiently high temperatures the hydrogen atom will have time to diffuse away before the electron drops back to its normal state, so that an F centre is left behind. The necessity for the H atom to diffuse away will account for the fact that the quantum-yield drops low values at low temperatures (Pohl, figure 28).

Prof. Pohl mentioned the fact, not stated in his report, that in the optical production of F' centres from F centres, the absorption of *one* quantum destroys *two* F centres and forms *two* F' centres. He suggested that the electron released from an F centre is recaptured *most easily* in the neighbourhood of another F centre, and that the two F centres so formed influence one another in such a way that they give the F' absorption spectrum. This hypothesis accounts for the fact (Pohl, figure 19) that the mean range of the liberated electrons is proportional to the number of F centres already present.

On the hypothesis given above we may assume that, in the potential hole caused by the removal of a negative ion, *two* electrons may be trapped, just as two electrons may exist in the potential hole of the proton to form a negative ion H^-. What the absorption spectra reveal as a pair of F' centres are thus two electrons trapped in the same potential hole. On the other hand this would suggest that all F' centres should have just the same absorption band.

In conclusion, it must be emphasized that the correctness of the model given above is by no means proved. Prof. Pohl stated that he liked it the best of the various models suggested, but that further experimental work was required before it could definitely be accepted.

Dr W. F. Berg gave an account of experiments by himself and K. Mendelssohn on photographic sensitivity at low temperatures. According to present-day conceptions the photographic latent image consists of a small speck of silver, which has been formed by a primary photoelectric process and secondary processes which mainly consist of flocking together of silver particles and of getting rid of the bromine. Without going into the mechanism of these processes one can say that they imply the transport of matter through the crystal lattice. This transport should not be possible at sufficiently low temperatures, since the mobility drops with temperature as an exponential function. This was the reason for undertaking a preliminary determination of the photographic sensitivity down to 20° K. (liquid hydrogen). Measurements have already been done at 90° K., e.g. by F. Luft (*Phot. Korr.* **69**, 161–5 (1933)) and S. E. Sheppard, E. P. Wightman, and R. F. Quirk (*J. phys. Chem.* **38**, 817–31 (1934)). Defining sensitivity as the exposure

necessary to give a density of 0·1 above fog it was found that (1) for a blue sensitive emulsion the sensitivity at 90° is 7 per cent, at 20° K. is 4 per cent of that at room temperature; (2) for a panchromatic emulsion at 20° the sensitivity is 0·4 per cent of the room temperature sensitivity for unfiltered tungsten light, 0·02 per cent for light filtered through a red No. 22 Wratten filter.

These results are in general agreement with the earlier papers as far as sensitivity at 90° is concerned. They have interest outside photography, which is possibly only a very sensitive means of studying the ionic conductivity in crystals. The sensitivity is surprisingly high in every case and can hardly be understood, if our conceptions are correct.

Prof. Pohl suggested that the actual transport of matter took place only after warming up.

Dr Berg also reported experiments on the print-out effect at 90° K. Solio paper gave a visible effect while still under liquid air, the sensitivity being reduced to about 10^{-5}. Slow Kodaline film gave no effect, the sensitivity being reduced to less than 10^{-6}.

ALKALI-HALIDE PHOSPHORS CONTAINING HEAVY METALS

By R. HILSCH, Göttingen

§ 1. INTRODUCTION

THIS paper is an account of some of the work on the alkali-halide phosphors carried out in the Göttingen laboratory. The phenomena are simplest in phosphors activated by heavy metal halides[1, 2], and the discussion of these will form the main feature of this paper.

These phosphors can easily be prepared by adding to the molten alkali halides small concentrations of the heavy metal halides; the crystal phosphors can then be produced as single crystals and then the light absorption caused by the heavy metals can be measured easily. In most cases the absorption lies in the range of wave-lengths for which the pure crystal is transparent.

In contradistinction to most of the known phosphors, we are here dealing with the simplest lattices, only one kind of foreign atom being embedded within the body of the crystal.

§ 2. THE ABSORPTION SPECTRA OF THE ALKALI-HALIDE PHOSPHORS

It is often held that in these phosphors a real mixed crystal is formed, the heavy metal ions replacing the alkali ions in the lattice. The following discussion shows that this hypothesis must be accepted with reserve.

Figure 1 shows an example of a silver phosphor, the absorption spectrum of KI with 0·05 per cent AgI[3]. A double band at 260 mμ. (at 20° C.) is observed to appear in the neighbourhood of the absorption edge of pure KI. At a temperature of 205° C., the band of longer wave-length alone is found. The behaviour with temperature of this transformation has been carefully investigated. With increasing temperature the intensity of the band at $\lambda = 265\,\mathrm{m}\mu$. increases continuously. The transformation is complete at 148° C. This is a remarkable fact, for at the same temperature AgI possesses a point of transformation[4]. In spite of the small concentration, the AgI structure is in some way still conserved within the KI crystal. The assumption that in the mixed crystals one silver ion replaces one alkali atom of the body crystal is thus ruled out.

The absorption bands of the phosphors so far produced, which contain the thallo-halides, are shown in figure 2[5]. As well as the sharpness of the bands (in contrast to the diffuse bands of pure thallo-halides), it is striking that the halogen ions of the body crystal determine the situation of both the bands. This behaviour also does not agree with the assumption of a simple mixed crystal. It

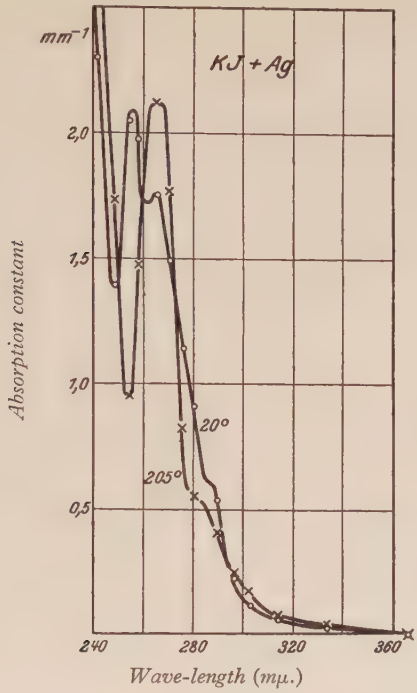

Figure 1. Absorption spectra of a KI phosphor activated by Ag above and below the transition point.

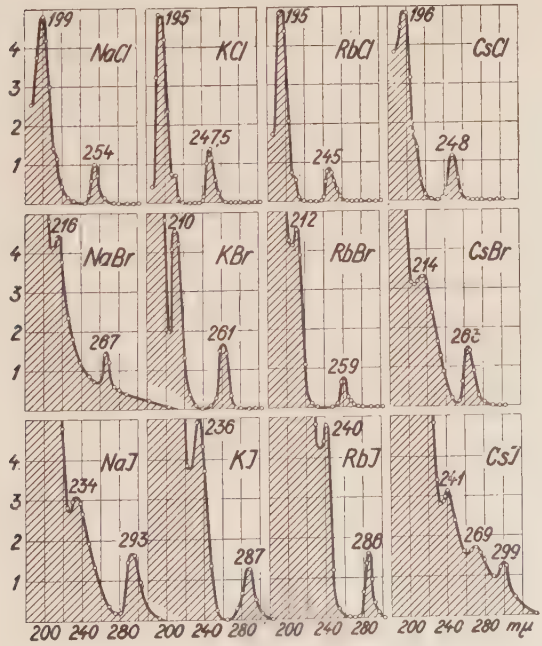

Figure 2. Absorption spectra of alkali-halide phosphors between 180 and 320mμ.

may also be mentioned that the small band in chloride phosphors lying at the foot of the short-wave band increases rapidly at high temperatures (over 500° C.) at the expense of the main band.[6] This also suggests a transformation of the lattice type of the centres responsible for the absorption. The distance between the two bands amounts in every case to about 1 eV. (In the case of chloride phosphors we take the band existing at high temperature.) This reminds one of the excitation energy of the thallium atom which is of the same value.

Similarly, measurements have been made of the absorption of alkali-halide phosphors with the addition of lead halides. The bands are found to be of the same sharpness. These will not be reproduced here. We must, however, stress the unimportant influence of the halogen ions and the determining influence of the alkali ions.

The phosphors activated by the copper halides do not show especially sharp regions of absorption. Moreover, in spite of a large addition of copper halides, only small amounts of copper can be actually dissolved in the atomic form. Several months later the absorption and with it the phosphorescent properties of the crystal are found to have disappeared almost completely, but they can be reproduced by a short period of heating[7,8].

Thus, the formation of phosphorescent centres is only possible through the application of force, and then only to a small extent.

§ 3. THE MECHANISM OF THE ABSORPTION BANDS

After having noted these facts, the mechanism of absorption still remains to be explained.

Some experimental researches of Fromherz, Menschick and Kun-Hou-Lih are of great importance[9,10,11]. Starting out from the already known absorption spectrum of alkali-halide phosphors, they investigated the absorption of the heavy metal halides in aqueous solutions. Besides the dissociated metal ions and the halogen ions, uncharged and positively charged molecules of the metal halides will be found in the solution, according to its concentration. The absorption bands of the aforesaid molecules have no similarity with those of the phosphors. When, however, we simultaneously add large quantities of the corresponding alkali halides (for example $H_2O + PbCl_2 + KCl$), we also find negatively charged complex ions (e.g. $PbCl_4$). The addition of alkali halides thus produces new absorption bands which may be ascribed to negatively charged complexes (MeX_n). The maxima of the bands of complex solutions, compared with those of crystal phosphors, are shown in table 1.

Table 1. Wave-lengths of absorption bands (mμ.)

	Crystal	Solution
NaCl + AgCl	210	216
KCl + CuCl	267	272
KCl + $PbCl_2$	273, 196	272, 195
KCl + TlCl	247, 196	242, —

The situation of the bands in solution as well as in the crystals is observed to be practically independent of the nature of the alkali chlorides. The bromides and iodides show the same behaviour.

From this Fromherz concluded that the active centres of the phosphors must have a structure similar to that of the saturated complexes. It must be supposed that within the crystal also there exists a rather isolated complex. This is easy to understand, when the great deformation produced by the heavy metal ion is taken into account. Thus we again approach the ideas put forward by Lenard and Schleede about the *Phosphoreszenzzentrum*.

§ 4. EMISSION BY ALKALI-HALIDE PHOSPHORS

We discuss only emission by thallium phosphors, which have been investigated thoroughly.

The emission consists of broad characteristic regions of emission with no remarkable structure. When illuminated with light of frequencies lying in the two absorption bands, the phosphors show fluorescence. On employing the radiation which is absorbed within the band at short wave-lengths, we also get phosphorescence up to 5 per cent. Fluorescence and phosphorescence give radiation with the same spectral distribution. One band, in particular, appears in the ultra-violet. The quantum yield, the decay of the after-glow and the spectral distribution of extinction have been closely investigated[12, 13, 14, 15]. The results are not simpler than those drawn from sulphide phosphors. The interpretation of the mechanism of emission has not yet been given. It is only in the case of the rare earth phosphors that Tomaschek and his collaborators have succeeded in ascribing the emission to the various states of foreign atoms.

The question of energy transition seems to be the most important one. As has been pointed out in the investigations of Gudden and Pohl[16], a photoelectric conduction appears parallel to the excitation and the emission of the phosphorescence of sulphide phosphors. The electrons ejected by the irradiation are free to move. In contrast to this, the alkali-halide phosphors never show photoelectric conduction, when irradiated with any wave-length[17]. We must conclude that in this case the electronic paths are very small and must be compared with the lattice distances. It is moreover certain that *F* centres will be produced by the accumulation of light-energy. We should suppose them to exist only in the vicinity of the *Zentrenkomplexe*.

In contrast to the absorption bands, the position of the emission bands depends upon the nature of the alkali ions of the body crystal. This is shown in table 2 for the thallium chloride phosphors.

Table 2. Maximum of the emission bands at 20° C. (mμ.)

NaCl	KCl	RbCl
288	300	315

Moreover, we find a considerable dependence upon temperature. The (TlX_n) complex must be considered if we are to interpret the emission bands. The excited states of these complex molecules, broadened by the energy of the lattice vibrations, are supposed to result in the unresolvable bands of the emission spectra. It is quite possible that these bands may be connected with the molecular spectra of thallo-halides investigated by Butkow[18]. (Here spectra in the same region of wave-length appear as those emitted by thallium phosphors.) Hence the light absorption in the thallium complexes should cause excited states of thallium-halide complexes, which are similar to those of molecules in the gaseous state. (As has already been pointed out, the distance between the thallium absorption bands in all crystals amounts to about 1 eV., equal to the excitation energy of thallium atom.)

If the TlX_n complex is responsible not only for absorption but also for emission, the complex in solution in water should also show fluorescence. A short time ago I found that this was in fact the case. A strong bluish-violet emission can be excited in an aqueous solution of LiCl + TlCl by illuminating it with light of wave-length 242 mμ., the wave-length of the first absorption band of the complex (TlX_n). The bands of bromides and iodides move still farther towards longer wave-lengths in the visible region. These results seem quite reasonable, for the surroundings of the complex also in the crystal influence the emission spectra, as we see from table 2.

§ 5. PHOSPHORS WITH NO ADDITION OF HEAVY METAL

It has lately been found that at high temperatures gases are able to diffuse in the form of molecules within the pure alkali halide[19,20]. During these researches two further phosphors were produced[21]. They were not activated by heavy metals, but by gaseous molecules, CO and O_2. Also in this case the absorption and emission must be ascribed to a complex. In the case of a crystal subject to a high pressure of O_2, ClO_4 might perhaps be the complex in question. The emission spectra are very remarkable. They consist of very sharp equidistant double bands. Their frequencies only depend to a small extent upon the body crystal used.

Until now it has not been possible to give a full explanation of these phenomena.

§ 6. SUMMARY

It is a remarkable fact that very complicated formations of molecules can be observed within the alkali halides in the form of single crystals. The luminescence processes which result from the construction of these complexes cannot as yet be interpreted. The exact process of absorption of light by the complex has also not been determined. Owing to their similarity with phenomena in aqueous solutions, however, the alkali halides have at least one advantage. Very definite complexes (MeX_n) may be shown to be responsible for the whole range of phenomena of light absorption and emission.

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THE EFFECTS OF TEMPERATURE ON THE INTENSITY OF FLUORESCENCE OF SOME IMPURITY SOLIDS

By J. T. RANDALL

Communication from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England

§ 1. INTRODUCTION

THE present paper is largely an account of some preliminary measurements on the effects of temperature on the intensity of fluorescence of a number of impurity solids under photoexcitation.

During the last few years it has become clear that the properties of fluorescent solids requiring the presence of impurities are closely linked with those of semi-conductors. The zone theory of electronic energy bands in crystals has been successful in explaining, not only many features of the properties of metals, but, in principle at any rate, some of the features of semi-conductors.

It is not unreasonable to suppose that the same theory, or some modification, will ultimately be of great value in the study of fluorescence. At the present time, however, the difficulties of determining the energy zones in crystals with quantitative accuracy are extremely great, as may be seen from the recent work of Shockley[1] and Ewing and Seitz[2] on the alkali halides. Nevertheless, it remains true that no model of a fluorescent impurity solid other than that which depends on the division of the electronic energies into zones has been seriously proposed. It will be remembered that in the application of this model to certain types of semi-conductor by Wilson and Fowler, a notable feature was the temperature-dependence of the conductivity.

Very little work has as yet been carried out on the temperature-dependence of the intensity of fluorescence. In starting this work it was felt that the results might in due course help to throw some light on the mechanism of fluorescence in impurity solids, and possibly on the interchange of energy between "free" electrons and the lattice atoms. It is clear from the complex nature of the results that a great deal remains to be done.

As will be seen in more detail below, the greater number of powders examined consisted of zinc sulphides, or zinc-cadmium sulphides in solid-solution, each with various activating impurities. In addition, alumina and cadmium iodide were examined. It is necessary here to say a little about the zinc sulphide type of fluorescent material.

It is of course well known that the fluorescence effects observed with sulphides are a result of the presence within the solid of minute traces of impurity.* In this they differ from the uranyl salts, for example, where the seat of luminescence is in the co-ordination group of the uranyl ion, and the luminescence spectra are essentially molecular in type[6]. It should also be noted that the sulphides, as distinct from the alkali halides considered by Hilsch[3], are photoconducting. The intensity of fluorescence of the sulphides is dependent, not only on the nature and amount of deliberate impurity, but on the complete exclusion of any other foreign material. In these compounds impurities to the extent of one or two parts in a million are frequently of vital importance whenever the details of the fluorescence spectrum have to be repeated with accuracy from specimen to specimen. In the silicates and phosphates, on the other hand, the optimum amount of impurity is frequently in the neighbourhood of from 0·1 to 1·0 per cent. From the point of view of the present experiments this means that one cannot assume that the only impurities present are those deliberately added at the outset of preparation; it is necessary to examine the final product spectroscopically in order to be reasonably sure of the total number of impurities. It was hoped at the start of this work to examine a number of zinc-cadmium sulphide solid-solutions, and also to compare the hexagonal and cubic varieties of zinc sulphide, all with the one impurity. The extreme ease with which sulphides of this group take up any extraneous impurity have made it impossible to carry out such an ideal programme, but the complexity of the results clearly suggests that further attempts in this direction will be worth while fundamentally.

Copious details for the preparation of fluorescent materials have been given from time to time[4], and it is only necessary to emphasize here one or two points of interest in connexion with the results which follow. The initial complex of pure matrix plus activating impurity has always to undergo a heat treatment in order that sensible fluorescence may subsequently be produced. It is also generally assumed that the activator during this treatment enters into solid-solution with the matrix. The work of Hilsch appears, however, to throw some doubt on this in the case of the alkali halides. The activating impurity is frequently added to the pure sulphide matrix in the form of a dilute solution to ensure adequate dispersion, and, theoretically, it should then only be necessary to heat the combination of the two to an appropriate temperature. While this procedure is successful with certain combinations of matrix and activator, others require the further addition of "fluxes". The avowed object of these is to promote crystal growth of the matrix and solid-solution of the main activator. Experiments show, however, that fluxes are frequently real impurities. Spectroscopic examination reveals their presence in the final material, and it is apparently impossible to remove them completely by means of washing processes.

* The work of Schleede[7] appears to show that strong blue fluorescence may be obtained from *pure* zinc sulphide, and the necessary condition for this is the presence of mixed crystals of wurtzite and blende. It is not improbable that the juxtaposition of the two types of crystal structure may be regarded theoretically as introducing at boundaries new levels which are effectively of the impurity type.

Before passing on to the experimental work a little must be said about the fluorescence spectra of impurity solids. Such spectra, where excited by ultra-violet, are characterized at room temperature by the presence of broad structureless bands, which may under certain special conditions be accompanied by very narrow bands with definite structure. The lowering of the temperature to that of liquid air, for example, results in a narrowing of the broad bands, but there appears to be no certain evidence that this is accompanied by development of structure within the bands.

The occurrence of very narrow bands, or even line systems, in the fluorescence spectra of impurity solids is usually due to the use of either chromium or one of the rare earths as activating impurity. The fluorescence spectra in cases of this kind are apparently partly made up of rather distorted line spectra of the ions of the activating impurities themselves. Presumably in this case the impurity levels lie just above the bottom of the conduction band. This aspect of the subject bears close resemblances to the work of Spedding[5] on the absorption spectra of rare-earth salts.

In the more normal cases of fluorescence with structureless bands, the impurity levels will lie within the forbidden zone. On this view it is easy to see why different solids require different exciting wave-lengths. In order to excite electrons into the conduction band the exciting wave-length must have an $h\nu$ value at least equal to that of the lowest energy values possible at the bottom of the conduction band. On this view the matrix lattice determines the exciting wave-length, and the impurity the fluorescence colour. In the well-known case of the ZnS/CdS sulphides with constant impurity the average wave-length of fluorescence increases as the cadmium content increases; it appears probable that this is due to the gradual lowering of the conduction band. Such ideas cannot at this stage be regarded as substantiated quantally; they merely serve to give a working picture of the process.

§ 2. SUBSTANCES EXAMINED AND EXPERIMENTAL PROCEDURE

The substances examined, together with the crystal lattices concerned and the impurities detected, are conveniently summarized in the following tables:

Table 1. Series of zinc sulphides

Powder and lattice details	Main impurities	Minor impurities*
(1) Cubic	Ag, Mg	Ba
(2) Hexagonal	Ag, Mg	Cd, Ba
(3) 75 % hexagonal, 25 % cubic	Ag, Mg	Cu, Ba, Ni
(4) Cubic	Cu, Mg	Cd, Ba
(5) Hexagonal—slightly contracted lattice	Mn	Ba, Si

* Detected spectroscopically as traces.

Table 2. Series of zinc-cadmium sulphides

Powder and lattice details*	Main impurities	Minor impurities
13 % CdS, 87 % ZnS	Cu, Mg	Ag
16 % CdS, 84 % ZnS	Cu, Mg	Ba
24 % CdS, 76 % ZnS	Cu, Mg	Ag, Ba
29 % CdS, 71 % ZnS	Cu, Mg, Al	Ag, Ba
33 % CdS, 67 % ZnS	Cu, Mg	Ag, Ba

* The percentages refer to molecular proportions.

Table 3. Cadmium iodide and alumina

Powder and lattice details	Main impurities	Minor impurities
Cadmium iodide	Pb	Ag, Cu
Alumina—corundum type	Cr	—

The first column of each table describes the lattice and the constitution of the material, with the exception of table 2 where all the lattices are of the hexagonal type; the term "cadmium iodide" is by now sufficient both to describe the material and the lattice type. In the second column are given the main impurities, and it should be said that these have been identified not only as those which were deliberately added, but also spectroscopically by arcing the powders on graphite electrodes. In all cases where magnesium occurs it was added as flux material, and this also applies to the traces of barium. Any other impurities recorded in the case of the sulphides are accidental, and such as are likely to be picked up in any chemical laboratory by sulphides. It should be added that the compositions of the zinc-cadmium sulphides were determined by means of their X-ray patterns after the final heating process. This is an important point, as cadmium sulphide very readily evaporates from the solid-solution, and it appears that this is the only accurate means of determining the nature of the final product.

Although from general experimental acquaintance with this type of material one would consider it unlikely that variations of crystal size and lack of homogeneity in the powders are of greater importance than the impurities themselves, the X-ray apparatus revealed the following further information.

Table 4. Further details of the zinc-cadmium sulphide series of table 2

Percentage of cadmium sulphide	Details of homogeneity, crystal-size, etc. obtained from X-ray photographs
33	Crystal size about average for Zn/Cd sulphides. Outer diffraction lines fuzzy, indicating distortion or lack of homogeneity
29	Similar to 33 % sample
24	Crystal size probably lower than above. Two distinct phases differing slightly in CdS content revealed by resolution of high angle diffraction line
16	Crystal size similar to 24 %. Uniform composition
13	Crystal size similar to 24 and 16 %. Two distinct phases, but very close together. Less difference than in 24 %, and one phase weaker than the other

Where two distinct phases occur, the difference in CdS content is of the order of 1 per cent.

The fluorescence of the materials examined was excited by means of a high pressure mercury-vapour discharge lamp in conjunction with a Woods Glass filter. The excitation was therefore essentially that of the 3650 A. triplet. The fluorescence intensity was measured by means of a rectifier type of photoelectric cell in series with a galvanometer. The sensitivity of the cell varies a good deal according to the particular spectrum irradiating it, and no attempt has been made in this preliminary work to correct for this. The object of the experiments was mainly to obtain the general shape of the fluorescence-intensity temperature curves. The results are not therefore on an energy basis, and the fact that two powders may give rise to a particular deflection on the galvanometer at a given temperature has no special significance. As will be seen below, the room temperature deflection was usually chosen arbitrarily. At the present stage, also, the small colour changes which occur in the fluorescence spectra as the temperature is changed have been neglected.

With regard to the heating and cooling of the specimens, two pieces of apparatus were used, one for temperatures between 90° and 400° K., and the other from room temperatures to any high temperature desired. The measurements do not in fact extend much beyond 600° K. It was usually arranged for the two sets of readings on a particular specimen to overlap in temperature, in order to be sure of the continuity of the curves. For the higher temperatures the powders were dusted on to a miniature hot-plate fitted with thermocouple. The temperature of the surface of the powder was not exactly the same as that registered by the thermocouple, and the readings taken on a rising temperature scale differed slightly from those taken when the plate was cooling. In the curves reproduced later the means of these two sets of readings are plotted in each case. For the lower temperatures, down to that of liquid oxygen, a small thin quartz tube was used. The tube was fitted with a ground joint, and the cooling liquid poured into the tube, the powder being on the lower part of the outer surface. To insulate the powder from the atmosphere, and also to avoid condensation of moisture on the cooled powder surface, the cooling vessel is surrounded by an outer jacket, which is provided with means for evacuation. In this way it was found that uniform temperature over the whole of the powder surface could be maintained. In front of the photocell were placed a water filter and a Wratten 2*a* gelatin filter to absorb any stray infra-red and ultra-violet. A set of readings was usually started by taking a "room temperature" deflection on the galvanometer with the ultra-violet source in a steady state. The distance of the source from the fluorescent specimen was then adjusted until the deflection was in a convenient region covered by the calibration curve of the photoelectric cell for different intensities of illumination. In the neighbourhood of room temperature water was normally used to aid the equalization of temperature over the surface of the inner tube. After removing the water, liquid air was poured into the inner tube and the equilibrium reading taken. The liquid air was then allowed to evaporate, and, just before this was achieved, a quantity of acetone at approximately the

freezing point was poured in. This enabled another "fixed" point on the curve to be obtained, and provided a means of obtaining a comprehensive set of readings between approximately 180° K. and room temperature as the cooling liquid warmed up. The series was then completed by a few readings overlapping with the hot-plate temperature range, and for this either hot water or paraffin was employed.

§ 3. EXPERIMENTAL RESULTS

The general results may be summarized very briefly, although some of the details of the various curves will require further discussion. It appears, for all the substances examined, that there is a critical temperature above which the fluorescence intensity always falls fairly rapidly and uniformly. At still higher temperatures the rate of decrease of intensity with temperature decreases. Below what has been called the critical temperature for convenience, a variety of things

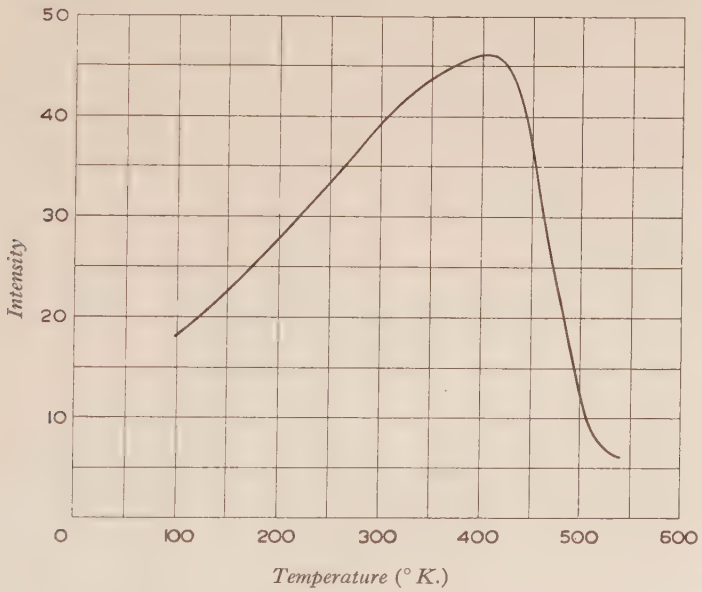

Figure 1. Zinc sulphide hexagonal. Impurities Mn, Mg, (Ba), (Si).

may happen. In certain cases the intensity may remain sensibly constant as the temperature is reduced; in others there may be a continuous fall; in the zinc-cadmium sulphides there are usually two maxima, and it is the higher temperature maximum that has been associated with a "critical" value of the temperature.

It is convenient to consider first of all the case of hexagonal zinc sulphide with manganese as the main impurity; this is the substance numbered (5) in table 1. For this the intensity variation with temperature appears to be of a fairly simple nature (figure 1). Starting at 100° K. the intensity rises almost linearly with temperature to a maximum value at about 400° K., followed by a sharper linear drop

in intensity. Finally at about 500° K. the curve flattens out. It should be noted that this particular powder has a slightly contracted lattice, due no doubt to the presence of manganese sulphide in solid-solution.

Turning now to the curves of figure 2, where the results for the remainder of the "pure" zinc sulphides are recorded, we see that they differ a good deal from those for the manganese-activated powder of figure 1. With the exception possibly of (3) the slopes of the high temperature portion of the curves is rather less, and the low temperature behaviour is considerably different. In three cases, those of powders (3), (4) and (2), there is a distinct small hump at low temperatures, while powder 1 has a minimum at about 180° K. It must be admitted that the complication of the multiple impurities makes it a difficult matter to be certain of the interpretation to be given, but one or two points may be made. First of all comparing powders (2) and (4), it is noticed that in spite of the difference in structure, and the difference in one of the main impurities, these curves are very similar in shape. We are led to

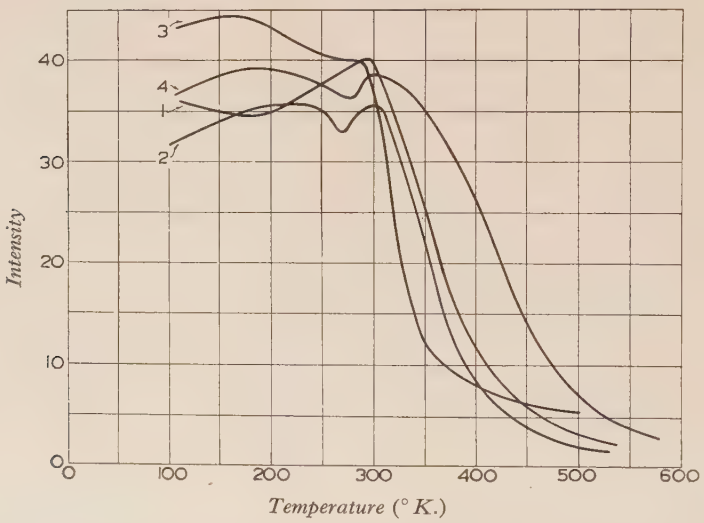

Figure 2. Effect of temperature on fluorescence of cubic and hexagonal ZnS with various impurities. (1) cubic ZnS, Ag, Mg, (Ba); (2) hexagonal ZnS, Ag, Mg, (Cd), (Ba); (3) hexagonal + cubic ZnS, Ag, Mg, (Cu), (Ba), (Ni); (4) cubic ZnS, Cu, Mg, (Cd), (Ba).

assume that in such similar crystal structures, the differences are not of importance, or, if they are, they have been conveniently smudged out by the difference in impurity. If the differences in structure are unimportant, then copper and silver appear to give very similar results. Assuming this, and turning to (1) on the same figure, the minimum in the low temperature part of the curve appears to be associated with the absence of cadmium.

In figure 3 are reproduced the curves for the solid-solutions of zinc and cadmium sulphides, and with the exception of curve (*e*), representing the 29 per cent cadmium solid-solution, the curves show strong similarities to curves (2), (4) and (3) of figure 2. It is to be noticed that Cu is a common impurity for all the specimens

of this series. Although silver is absent only from (*c*) with 16 per cent CdS, its absence makes no general difference to the shape of the curve, which is essentially similar to curve (*a*), which is curve (4) of figure 2 reproduced here for comparison. A further point of interest is that the low temperature peak becomes more pronounced as the proportion of cadmium is increased. In curve (*e*) this peak quite

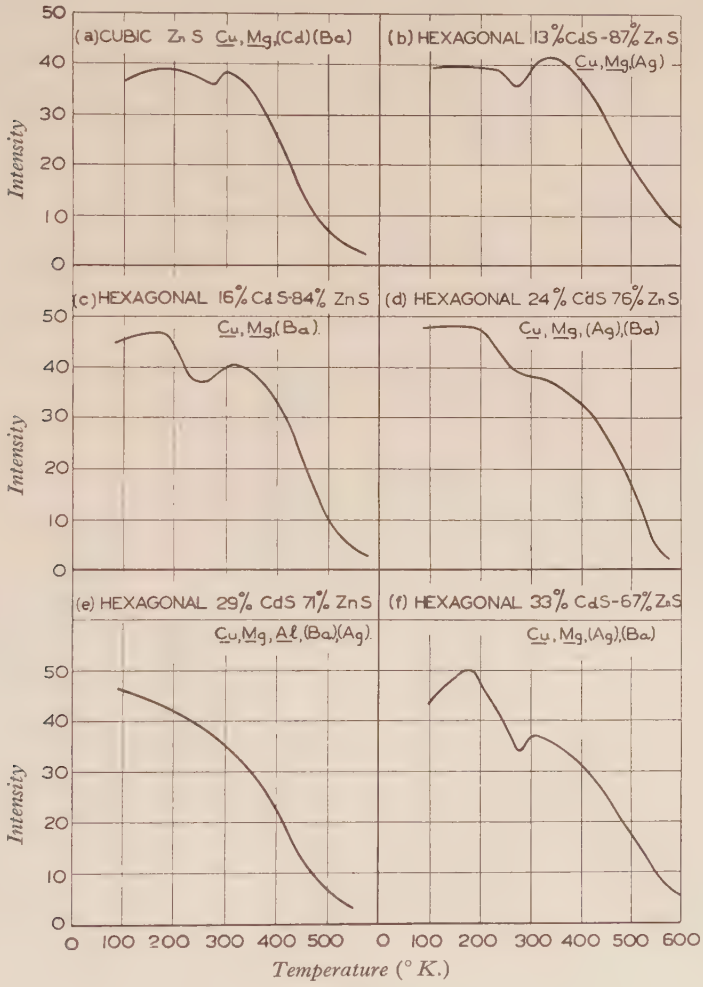
(a) CUBIC ZnS Cu, Mg, (Cd) (Ba)
(b) HEXAGONAL 13% CdS-87% ZnS
Cu, Mg, (Ag)
(c) HEXAGONAL 16% CdS-84% ZnS
Cu, Mg, (Ba)
(d) HEXAGONAL 24% CdS 76% ZnS
Cu, Mg, (Ag), (Ba)
(e) HEXAGONAL 29% CdS 71% ZnS
Cu, Mg, Al, (Ba), (Ag)
(f) HEXAGONAL 33% CdS-67% ZnS
Cu, Mg, (Ag), (Ba)
Intensity
0 10 20 30 40 50
0 100 200 300 400 500 0 100 200 300 400 500 600
Temperature (° K.)

Figure 3.

dwarfs the room temperature peak. In the case of the 29 per cent CdS of (*e*) it is interesting to note that the single curve obtained has no obvious peak and appears to be associated with the presence of a certain amount of aluminium; it is possible that a new peak has been inserted between 250° and 300° K. which has had the effect of smoothing out the curve in this way. The more general significance of these results will be considered later.

Meanwhile it remains to indicate the results on two rather different types of

luminescent material; for it was felt advisable even at this stage that experiments on as many different types as possible would be of help in the general interpretation. Figure 4 shows the effect of temperature on the fluorescence of cadmium iodide activated by lead, with minor traces of Ag and Cu present. The intensity is fairly

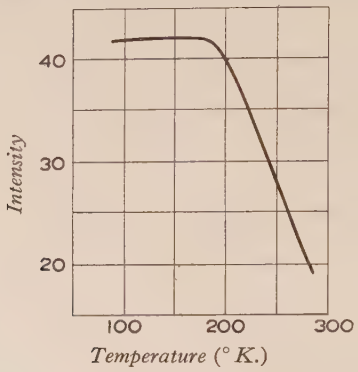

Figure 4. Cadmium iodide, CdI_2; impurities Pb, (Ag), (Cu); yellow fluorescence.

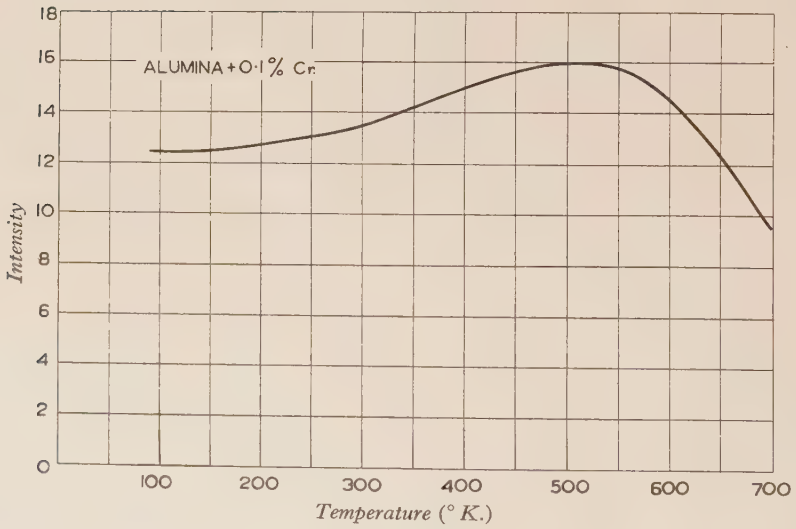

Figure 5. Alumina activated by chromium.

constant at low temperatures but this is followed by a steep and linear fall at about 200° K.

So far, luminescent materials with the broad structureless type of band spectrum only have been considered. In figure 5 is given the curve for alumina activated by chromium. The luminescence spectrum of this material taken at room temperatures consists of a number of rather broad lines together with a rather weak intensity general background. The lines have been attributed by Tomaschek and

Deutschbein to triply ionized chromium. The intensity curve is somewhat similar to that of the hexagonal zinc sulphide of figure 1, except for the rather flat portion at low temperatures. It should also be noted that the maximum in the curve occurs at a much higher temperature, viz. 500° K., than for any others so far examined.

§ 4. DISCUSSION OF RESULTS

While it must be stressed that the present results are only the preliminaries of a rather wider investigation and that minor details may be altered by further work, it is felt that some points of rather general significance may already be deduced from them.

In the first place there is no strong evidence that the change from cubic to hexagonal zinc sulphide produces any marked changes in the intensity curves. It has already been pointed out that the intensity of the low temperature peak of the zinc-cadmium sulphides relative to that of the "high" temperature peak depends to a marked extent on the proportion of cadmium present. This could clearly be ascribed to the gradually changing lattice constant as the amount of cadmium increases, were it not for the fact that in the zinc sulphides the same low temperature peak, present on a rather diminished scale, appears also to depend on the presence of cadmium not as a bulk constituent, as in the solid-solution, but as a minor impurity. This low temperature peak must therefore be associated with the cadmium, and the suggestion is, that even in those powders where the cadmium is already present in bulk, the cadmium, possibly in some other form, is also acting as an important impurity from the point of view of fluorescence. There is nothing particularly objectionable in this idea, as it has been used to explain the behaviour of certain semi-conductors. It is however new as far as the subject of luminescence is concerned, and it remains to be seen what is the exact significance physically of the association of the cadmium as an impurity with the so-called principle activators such as copper and silver. This point is particularly interesting in view of the fact that the X-ray results for the solid-solutions record the definite presence of inhomogeneities.

The curves of figures 2 and 3 were obtained prior to those of figure 1, and their strangely varying slopes at low temperatures were somewhat puzzling at first sight.

The results shown in figure 1, however, together with those on alumina and the known nature of the spectra of the materials, give the general clue.

The susceptibility of all luminescent sulphides to traces of extraneous impurity leads to the presence, in general, of more than one broad band in the fluorescence spectrum. In figures 2 and 3 we appear to be witnessing the superposition of the temperature curves for more than one band. Occasionally, when it is possible to produce a powder with one chief activating impurity, a decidedly simple type of temperature curve results, and this simplicity is shown in figures 1 and 5 in spite of the rather different types of spectra.

It is interesting that all the substances examined show on the high temperature side a rather steep slope, and this rather confirms our view. From the

theoretical standpoint there is presumably no difficulty in accounting for the presence of a number of fluorescence bands. One of the problems will be to account for the dependence of the band intensity on temperature, the chief characteristics being a positive slope at low temperatures, followed by a negative slope at higher values of T. At the present time it appears rather easier to understand the high temperature part of the curve. As the temperature increases a decreasing fraction of the total number of excited electrons becomes available for radiative transitions to lower levels. There is at present no evidence to show whether these electrons remain in the upper band, or whether their energy is increasingly lost by collision with lattice atoms as the temperature rises. From the experimental standpoint it is important to determine to what extent the absorption of ultra-violet remains constant over the temperature range considered. I am indebted to Dr Peierls for pointing out the two aspects of this problem: the possible variation of average absorption with temperature, and the dependence of absorption on the nature of the exciting spectrum. Until answers concerning these points have been obtained, no further certain conclusions may be reached from the present experiments.

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DISCUSSION OF THE PAPERS BY HILSCH AND RANDALL

Reported by N. F. Mott

In reply to questions, Dr Hilsch emphasized that photoconductivity was observed in sulphide phosphors, but not in the alkali halides. But in the latter case photoconductivity did not seem to be intimately connected with phosphorescence; the electrons are not removed to any very large distances. Prof. Pohl suggested that *if* there exists a phosphorescence with a long decay period, *then* we may suppose that the electron responsible for the radiation is removed by the absorbed quantum a long way from its original position, i.e. a distance of many atomic diameters. But in the other type of phosphor, in which the electron is not removed, the light absorption causes the transformation of one type of molecule into another; the initial and final states being distinguished for instance by a difference of crystal

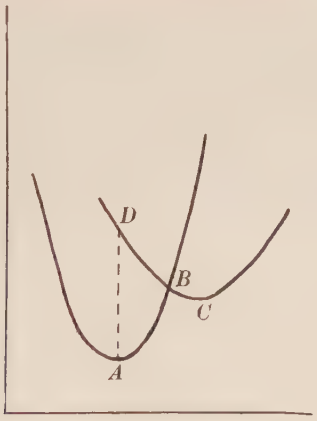

Figure 1.

form—i.e. by the atomic nuclei taking up new positions. Prof. Pohl also emphasized the importance of making large crystals of the sulphide phosphors in order to understand their properties.

Prof. Mott and Dr de Boer discussed the mechanism by means of which a molecule in a crystal could re-emit light after a period of minutes or hours. Figure 1 shows the energy of the normal and excited states of the molecule plotted against some parameter d representing the configuration of the atoms of the molecule; for example, the distance between two of the atoms. A molecule originally in the state A absorbs, by the Franck-Condon principle, light having the quantum energy AD. The molecule then moves into the more stable state C, in which it cannot radiate.

Thermal agitation might cause the molecule to come into the state A, whence it could descend to A giving up its excess energy as heat, or, owing to the finite velocity of motion of the ions, it might ascend towards D and thus have a chance to radiate. The resulting band would however have its maximum at very large wave-lengths.

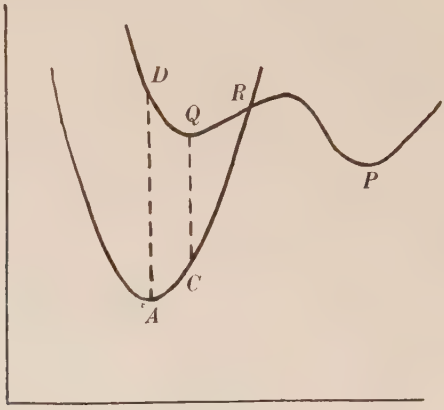

Figure 2.

The more complicated mechanism shown in figure 2 seems necessary in order to account for an emission band in the visible, the upper curve having two minima. After absorption the large amount of energy released takes the molecule to P, where it cannot radiate. If then thermal energy raises it to R, it will drop down to Q, where it will remain until it radiates a quantum of energy QC.

Mr J. Ewles gave an account of experiments on phosphorescence carried out at Leeds. These will be published in the *Proc. roy. Soc.**

* See also Ewles, *Proc. roy. Soc.* A, **129**, 509 (1931), *Proc. Leeds Phil. Soc.* **3**, 277 (1936).

SEMI-CONDUCTORS WITH PARTIALLY AND WITH COMPLETELY FILLED 3*d*-LATTICE BANDS

By J. H. DE BOER and E. J. W. VERWEY,
Natuurkundig Laboratorium der N. V. Philips' Gloeilampenfabrieken,
Eindhoven, Holland

ABSTRACT. Attention is drawn to a class of semi-conductors or insulators with incompletely filled 3*d* bands. Their lack of conductivity, if the number of electrons per atom is an integer, is explained by the circumstance that a moving electron will have a large probability of being withdrawn to the initial atom, if only the potential barriers to be penetrated are sufficiently high to reduce the frequency of transition below a certain limit. This inhibiting factor disappears, if for ions of equal electronic levels the number of electrons per atom differs from an integer. In the case of NiO this condition is fulfilled if an electron is brought by thermal excitation from the lattice 3*d* band into the somewhat raised and less occupied levels *a*, *a'* (figure 1); these levels belong to Ni ions adjacent to a vacant Ni lattice point introduced by the deviations from stoichiometry, and two of these Ni ions are at the absolute zero Ni^{3+} ions. An analogous conduction mechanism holds for non-stoichiometric Cu_2O, with a completely filled 3*d* band (figure 2).

Photoconductivity is generally observed with substances with completely filled zones and never with substances of the NiO type. A tentative explanation is given for this fact on the basis of the model of figure 1 and figure 2.

In non-stoechiometric ZnO vacant oxygen lattice points are assumed (figure 3); in that case the calculation of the lattice levels shows that at the lattice holes one Zn^{2+} is converted into Zn, whereas in the lattice the additional electrons form Zn^{+} ions, as will be the case after thermal transitions of the electrons belonging to these Zn atoms into the lattice 4*s* band.

§1. CLASSIFICATION OF SEMI-CONDUCTORS

According to the quantum theory of electronic states in solids, as developed by Sommerfeld, Bloch, Brillouin, Bethe and others[1,2,3], with the special aim of understanding the electrical properties of the metals, those substances will be electrical insulators for which the number of electrons is just sufficient to fill up a number of Brillouin zones completely, and the lowest unoccupied Brillouin zone is separated from the occupied zone with the highest energy by a sufficiently broad energy gap (forbidden region). For instance the following ionic compounds NaCl, MgO, AgCl, ZnO, TlCl all contain only ions with closed electronic groups or sub groups and thus only completely filled Brillouin zones, and they are known to be very poor conductors if they are pure and of stoichiometric composition. Though, according to quantum mechanics, all the electrons of a perfect lattice are more or less free to move through the lattice, the electronic states of a completely filled energy zone cannot give rise to electronic conduction, and unidirectional transport of electrons is only possible if a zone is incompletely filled, either because the number

of electrons is incapable of filling up the zones completely, or because several zones overlap in the lattice, the electrons of one atomic level being thus distributed over more than one band or zone of lattice levels. On the basis of these conceptions Wilson[4] and Fowler[5] have developed a theory of semi-conductors. Wilson considers the case of two energy zones, one exactly full of electrons at absolute zero and a higher one entirely empty, separated by a narrow forbidden region. Accordingly at a higher temperature there will be a few electrons of the lower zone in the higher one, and necessarily a number of empty states in the lower zone. Both will give rise to electronic conduction, but predominantly the electrons in the higher zone, where the potential barriers are lower with respect to the electronic levels. Such semi-conductors, which owe their conductivity to thermal excitation of electrons from one energy zone into another higher one, were called *intrinsic* semi-conductors.

A substance belonging to the class of semi-conductors in which electronic conduction occurs predominantly according to the model of Wilson is probably Cu_2O of stoichiometric composition. In this compound the cuprous ion Cu^+ contains a closed $3d$ shell and an empty $4s$ shell.

Sometimes insulators of the type considered above can be converted into semi-conductors in two ways, either by small deviations from stoichiometric composition or by foreign impurities. Of these *extrinsic* semi-conductors only the first mentioned will be considered in the present discussion.

(*a*) There exists, however, a large class of semi-conductors of a quite different type, for which it has only been recognized incidentally that they must be treated in a way deviating fundamentally from the Wilson theory. Several substances contain atoms or ions with an odd number of electrons; then, in many cases, at any rate for substances with a simple lattice type (such as simple translation lattices, or lattices with a face centred or body centred unit cell), the amount of electrons is incapable of filling up a number of Brillouin zones completely and we have to deal with a partially occupied Brillouin zone. Nevertheless several substances, especially ionic compounds, of this type do not show a metallic conductivity, but belong to the class of semi-conductors or even insulators.

In the present paper we will restrict ourselves to compounds containing ions of the first long series of the periodic system. As examples may be mentioned MnO ($\log \rho = 8$), CoO ($\log \rho = 8$), Mn_3O_4 ($\log \rho = 7$), Fe_2O_3 ($\log \rho = 10$), CuO ($\log \rho = 7$) etc.* The electronic configurations of the cations involved can be read from table 1. This table, comprising elements which have the argon configuration $(1s)^2; (2s)^2 (2p)^6 (3s)^2 (3p)^6$ in common, shows the distribution of electrons between the $3d$ and $4s$ shells for a number of important atoms and ions from the part of the periodic system considered. These distributions can be derived in some cases from the spectroscopical data[6] concerning the ground state of the free atoms or ions (shown in bold-faced type) and the remainder can then be derived by interpolation or (and) by taking into account the paramagnetism of the ions in the corresponding salts[7]. From table 1 it results that all ions present in stable chemical compounds

* The $\log_{10} \rho$ values (ρ = specific resistance in ohm-cm.) are only given as integers because of the inevitable uncertainty in these data; for our considerations only the order of magnitude is significant.

in the transition region of the periodic system considered contain $3d$ electrons and no $4s$ electrons. As a consequence of this circumstance we infer that there is no great difference between substances like those mentioned above, containing odd

Table 1

Atomic number of atoms / ber of trons ion	18	19	20	21	22	23	24	25	26	27	28
	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$	$3d$ $4s$
18	Ar **0 0**	K^+ **0 0**	Ca^{2+} **0 0**	Sc^{3+} **0 0**	Ti^{4+} **0 0**	V^{5+} **0 0**					
19		K **0 1**			Ti^{3+} **1 0**	V^{4+} **1 0**					
20			Ca **0 2**		Ti^{2+} 2 0	V^{3+} **2 0**					
21				Sc **1 2**	Ti (2) (1)	V^{2+} **3 0**	Cr^{3+} 3 0	Mn^{4+} **3 0**			
22					Ti **2 2**	V^+ **4 0**	Cr^{2+} 4 0	Mn^{3+} 4 0			
23						V **3 2**	Cr^+ **5 0**	Mn^{2+} 5 0	Fe^{3+} 5 0	Co^{4+} 5 0	
24							Cr **5 1**	Mn^+ **5 1**	Fe^{2+} 6 0	Co^{3+} 6 0	Ni^{4+} 6 0
25								Mn **5 2**	Fe^+ 6 1	Co^{2+} 7 0	Ni^{3+} 7 0
26									Fe **6 2**	Co^+ **8 0**	Ni^{2+} 8 0
27										Co **7 2**	Ni^+ **9 0**
28											Ni **8 2**

numbers of electrons, and for instance NiO, with even numbers of electrons, since the band of $3d$ levels contains five $3d$ zones and these $3d$ levels, coinciding in the free ions, presumably are not split up wholly into separate zones in the lattice, and all ions with an incompletely filled $3d$ group will therefore give rise to partially occupied energy bands in the lattice. Actually there is no great difference in the behaviour of CoO and NiO; for the latter also $\log \rho = 8$.

(*b*) Not all substances of the type considered are poor conductors. It is a well-known fact that both the conductivities of Cu_2O, CuJ, ZnO (with cations having a complete $3d$ shell, $3d^{10}$) and of CoO, NiO etc. (incomplete $3d$ shell) can be raised several powers of ten by small deviations from the stoichiometric composition[8, 9, 10, 11] and it has already been suggested by Wagner that this increased conductivity is connected with quasi-free electrons or electron holes owing to the presence of ions of higher or lower valency. A very interesting case is represented by Fe_3O_4 ($\log \rho = -2$), which has a conductivity of about ten powers of ten as high as Mn_3O_4, Co_3O_4, γ Mn_2O_3, γ Fe_2O_3.

In a previous publication we have shown that the cation arrangement in the

lattice of Fe_3O_4 shows an "averaged structure" of a special type, viz. a statistical distribution of equal amounts of Fe^{2+} and Fe^{3+} ions about crystallographically identical lattice points[12, 13]; in this respect it differs from Co_3O_4, γ Fe_2O_3, etc. with otherwise identical or closely related crystal structures (spinel type). From this we infer that favourable conditions for electronic conduction exist, if for a band of electronic states the number of electrons per atom (ion) differs from an integer, and this is also important in relation to the conductivity of non-stoichiometric compounds.

(*c*) A third point, which seems to be of some importance for a comprehension of the behaviour of the substances considered, is that only those substances (stoichiometric and non-stoichiometric) show photo-conductivity, which are derived from compounds with cations containing a complete 3*d* shell, viz. CuJ, Cu_2O, ZnO. This seems to be a general rule throughout the whole periodic system, since all substances reported to be photoconductors (halides of the alkali- and alkaline earth metals and of Ag^+, Cu^+, Tl^+, Hg^{2+}, Pb^{2+}; very many sulphides, e.g. Ag_2S, Sb_2S_3, HgS, Bi_2S_3, PbS, Ag_3SbS_3; oxides like BaO, Cu_2O, Ag_2O, CdO, Sb_2O_3) contain cations (and anions) with closed electronic groups or sub-groups. No photoconductivity has been observed, as far as we know, for substances like MnO, CoO, NiO, Co_3O_4, Mn_3O_4, Fe_2O_3 etc.; in this laboratory Mr H. H. Kraak has investigated certain of these compounds* by irradiation with a high pressure mercury discharge lamp and has been unable to establish any effect upon their conductivity.

From this discussion, then, a number of interesting points result, which can be summarized in the following three problems:

(1) Why are several of the oxides considered here semi-conductors or almost insulators, although they contain an incompletely occupied 3*d* band?

(2) Why do exceptionally favourable conditions for electronic conduction arise if the number of electrons per atom in this band is different from an integer?

(3) What is the reason why all these substances do not show photoconductivity, whereas those substances containing a completely filled 3*d* band are all photoconductors?

In the following sections we shall consider these substances from the point of view of their electronic bands and the relations between them.

§ 2. LATTICE DEFECTS

The nature of the lattice deviations involved in deviations from the stoechiometric composition and their significance for electronic conduction have been discussed in detail by Wagner[10]. Also in our case we must consider beforehand what changes occur in the lattices of the substances investigated, if the composition is made different from stoichiometry. For our present purpose, we need not consider the small deviations from the perfect lattice, which are present in every real lattice owing to the thermal equilibrium corresponding to the previous thermal history[14].

* Namely NiO, NiO containing some oxygen in excess, Co_3O_4 and Mn_3O_4 as pressed bars.

Greenish NiO can be transformed by oxidation into black "NiO" and then contains a small amount of oxygen (e.g. 0·5 per cent) in excess. The extra oxygen may be located between the normal lattice ions (interlattice points), but owing to the small polarizability of the oxygen it is much more likely that the lattice contains vacant nickel lattice points, whereas the additional oxygen is located at normal lattice points. This view is substantiated by the work of Jette and Foote[15], who investigated the crystal structure of Wüstite ("FeO"). A phase of pure FeO is not stable under any conditions; for the Wüstite phase, if prepared at 1050°, they found solid solutions containing 76·7–76·1 per cent Fe, i.e. from $Fe_{0.94}O$ to $Fe_{0.91}O$. These phases contain vacant positions in their cation lattice; the latter phase for example contains therefore an averaged distribution of $\frac{8}{11}$ Fe^{2+}, $\frac{2}{11}$ Fe^{3+} and $\frac{1}{11}$ vacant lattice points per oxygen ion about the normal cation position.* Also pure NiO seems to be unstable[16], and identical relations may be expected here, though the deviations from stoichiometry are less than in the case of FeO.

For NiO with an oxygen excess we must therefore assume vacant points in the cation lattice. Such an assumption can also safely be made for the case of CuJ with a small excess of iodine, in view of the large radius of the J^- ion. For Cu_2O the same view has been advocated by Dünwald and Wagner[17]. It has generally been assumed in these substances containing a metal deficit that the excess of negative charge originating from the excess of anions is neutralized at the cations, i.e. by the formation of cations of higher valency (Fe^{3+}, Ni^{3+}, Cu^{2+}); in the present cases this conception seems quite reasonable on the basis of chemical arguments, but the possibility that anions of a lower charge (eventually neutral atoms) are formed cannot be excluded *a priori*. Indeed, in KJ containing a small excess of iodine, no K^{2+} ions but J atoms are formed. This can easily be ascertained, however, for every case, by considering to what extent the various electronic levels are shifted in the lattices: the electrons will be removed from the *highest occupied* level. The results of such calculations are summarized in table 2. These calculations yield, of course, the positions that the levels would have, if they were not broadened by the lattice (in the following we denote these positions as "centres" of the bands). We also include the calculations of the electronic levels of ions adjacent to a vacant lattice point, for electrons must be removed as a consequence of the disappearance of a number of cations from the lattice and it is generally more favourable to remove these electrons from a cation that is adjacent to such a lattice hole. For the case of Cu_2O Schottky and Waibel[18] assumed therefore that Cu^{2+} ions are located directly adjacent to a vacant Cu^+ lattice position. For instance, for NiO (NaCl lattice type), where each vacant Ni point is surrounded by 12 nickel ions, we wish to consider the case that two of these nickel ions yield an electron and become Ni^{3+} ions, in order to counterbalance the absent Ni^{2+}. Neglecting polarization energies we see that such a Ni^{3+} is surrounded by a normal lattice minus one Ni^{2+} at a distance $r\sqrt{2}$ (r = shortest Ni-O distance) and plus one positive charge at $2r\sqrt{2}$ (in the most favourable state), hence the *Madelung* energy for one electron at the lattice point considered (Ni^{3+} ion

* Another possibility is that the Fe^{3+} seek different interstices, but presumably it can be excluded by the fact that no complete series of solid solutions with Fe_3O_4 exists.

Table 2

NiO			
Lattice type: NaCl,	$a = 4{\cdot}17$ A.	*Lattice:*	
Shortest distance Ni to O	$= 2{\cdot}09$ A.	*Madelung* energy (M)	$= 24{\cdot}2$ V.
Distance Ni^{3+} to lattice hole	$= 2{\cdot}98$ A.	Level Ni^{2+} $3d = M - I_3$	$= -\ 6$ V.
Distance Ni^{3+} to Ni^{3+}	$= 5{\cdot}96$ A.	Level O^{2-} $2p = -M - E_2$	$= -14$ V.
Madelung constant	$= 1{\cdot}748$	*At lattice hole:*	
Third ionization energy Ni (I_3)	$= ca.\ 30$ V.	*Madelung* energy Ni^{2+} (M'_{Ni})	$= 31{\cdot}6$ V.
Second electron affinity O (E_2)	$= -10$ V.	*Madelung* energy O^{2-} (M'_O)*	$= 13{\cdot}8$ V.
		Level Ni^{2+} $3d = M_{Ni}' - I_3$	$= +1$ V.
		Level O^{2-} $2p = -M_O' - E_2$	$= -3{\cdot}8$ V.
CuJ			
Lattice type: cubic ZnS,	$a = 6{\cdot}05$ A.	*Lattice:*	
Shortest distance Cu^+ to $J^- = \frac{1}{4}a\sqrt{3}$	$= 2{\cdot}62$ A.	*Madelung* energy (M)	$= 9{\cdot}0$ V.
Distance Cu^+ to lattice hole $= \frac{1}{2}a\sqrt{2}$	$= 4{\cdot}27$ A.	Level Cu $4s = M - I_1$	$= +1{\cdot}2$ V.
Madelung constant	$= 1{\cdot}639$	Level Cu^+ $3d = M - I_2$	$= -11{\cdot}2$ V.
First ionization energy Cu (I_1)	$= 7{\cdot}8$ V.	Level J^- $5p = -M - E$	$= -12{\cdot}1$ V.
Second ionization energy Cu (I_2)	$= 20{\cdot}2$ V.	*At lattice hole:*	
Electron affinity J (E)	$-3{\cdot}1$ V.	*Madelung* energy Cu^+ (M'_{Cu})	$= 12{\cdot}4$ V.
		Madelung energy J^- (M'_J)	$= 3{\cdot}5$ V.
		Level Cu^+ $3d = M'_{Cu} - I_2$	$= -\ 7{\cdot}8$ V.
		Level J^- $5p = -M'_J - E$	$= -\ 6{\cdot}6$ V.
ZnO			
Lattice type: hexagonal ZnS,	$a = 3{\cdot}25$ A.	*Lattice:*	
	$c = 5{\cdot}23$ A.	*Madelung* energy (M)	$= 23{\cdot}9$ V.
Shortest distance Zn to O	$= 1{\cdot}98$ A.	Level Zn^+ $4s = M - I_2$	$= \ 6{\cdot}0$ V.
Distance Zn to Zn	$= 3{\cdot}25$ A.	Level Zn $4s = 2M - I_1 - I_2$†	$= 20{\cdot}5$ V.
Madelung constant	$= 1{\cdot}639$	Level $O^{2-} = -M - E$	$= -13{\cdot}9$ V.
First ionization energy Zn (I_1)	$= 9{\cdot}4$ V.	Lowest member	
Second ionization energy Zn (I_2)	$= 17{\cdot}9$ V.	$O^{3-} > -13{\cdot}9 + \frac{2\epsilon^2}{r_{O^{2-}}}$‡	> 8 V.
		At lattice hole:	
		Madelung energy Zn^+ (M')§	$= +13{\cdot}7$ V.
		Madelung energy Zn (M'')	$= +\ 9{\cdot}3$ V.
		Level Zn^+ $4s = M' - I_2$	$= -\ 4{\cdot}2$ V.
		Level Zn $4s = 2M'' - I_1 - I_2$	$= -\ 8{\cdot}7$ V.
KJ			
Lattice type: cubic NaCl,	$a = 7{\cdot}05$ A.	*Lattice:*	
Madelung constant	$= 1{\cdot}748$	*Madelung* energy (M)	$= \ 7{\cdot}2$ V.
Distance K to J	$= 3{\cdot}53$ A.	Level K^+: $M - I_2$	$= -24{\cdot}5$ V.
Distance K to K $= \frac{1}{2}a\sqrt{2}$	$= 4{\cdot}99$ A.	Level J^-: $-M - E$	$= -10{\cdot}3$ V.
Second ionization energy K (I_2)	$= 31{\cdot}7$ V.	*Adjacent to failing* K^+	
		Madelung energy K^+ (M')	$= \ 10{\cdot}1$ V.
		Level K^+: $M' - I_2$	$= -21{\cdot}6$ V.
		Madelung energy J^- (M'')	$= \ 3{\cdot}1$ V.
		Level J^-: $M'' - E$	$= -\ 6{\cdot}2$ V.

* For two O^- ions adjacent to a vacant Ni^{2+} lattice point.
† For two electrons at one Zn^{2+} lattice ion.
‡ If an electron is added to O^{2-} there are no discrete levels; the lowest member of the continuum will be at least $2\epsilon^2/r_{O^{2-}} = 22$ V. higher ($r_{O^{2-}} = 1{\cdot}3$ A. = radius of O^{2-}).
§ For two Zn^+ ions adjacent to a vacant oxygen lattice point.

adjacent to a vacant Ni^{2+} point) amounts to ($A = Madelung$ constant):

$$\frac{2A\epsilon^2}{r} + \frac{2\epsilon^2}{r\sqrt{2}} - \frac{\epsilon^2}{2r\sqrt{2}} = 24{\cdot}2 + 9{\cdot}8 - 2{\cdot}4 = 31{\cdot}6 \text{ volts}$$

The electronic level of these ions is therefore raised 7·4 volts with respect to normal lattice ions, or rather considerably less owing to several polarization effects. The other data are calculated in a similar way.

In the case of ZnO the deviation from stoichiometry causing electronic conductivity is an excess of Zn. In the analogous case of BaO it has been shown that the red BaO containing an excess of about 1 per cent Ba has a density of about 0·5 per cent less than that of normal BaO[19]. We will therefore assume in BaO and similar substances that the excess of metal is present at normal lattice points, whereas a number of oxygen lattice points is vacant, though, for the case of ZnO, the possibility cannot wholly be excluded that Zn takes interlattice points, since Zn is more polarizable than Ba, and ZnO has a different lattice type. In the case of ZnO extra electrons must be introduced and we must therefore consider the *lowest unoccupied* level in the lattice and at lattice holes. From table 2 we make the following inferences.

For NiO with oxygen excess: both in the normal lattices as well as at lattice holes the removal of electrons leads to Ni^{3+} ions and never to O^- ions.

For CuJ with iodine excess: in the normal lattice Cu^{2+} are formed; adjacent to vacant Cu^+ lattice points the highest occupied level seems to be J^- and therefore J atoms are formed; the latter conclusion is somewhat uncertain owing to the high polarizabilities of the ions involved.

For ZnO with metal excess, assuming vacant oxygen lattice points: adjacent to an absent O^{2-} ion the lowest unoccupied level is that for a Zn atom. In the regular lattice, however, an excess of electrons yields a more uniform distribution of the electrons and leads to Zn^+ ions. The formation of O^{3-} can be excluded.

For KJ with iodine excess: the electrons are always removed from J^- ions.

§3. MECHANISM OF CONDUCTION

We now proceed to a consideration of the mechanism of electronic conduction. The theory of electronic states in metals has been developed on the basis of the assumption that the interaction of the electrons and ions of the lattice can be approached by treating each electron as moving in the field of the ions and the average field of all other electrons. This method of approach implies that all atoms (ions) of a definite kind contain an equal number of electrons, or, since electron movement must necessarily alter the number of electrons of an atom temporarily, that local charge differences are neutralized by other electrons within a short time; in other words that the electrons are free to such an extent that they can still be considered as *not* belonging to definite atoms. If the potential barrier between the atoms (ions) of one kind is increased the probability of interchange of electrons decreases rapidly and the time lag mentioned above increases. Thus, for somewhat higher potential barriers the state of affairs is finally fundamentally different

in metallic conduction. There is a certain probability that an electron leaks through a potential barrier to a neighbouring atom, say from one Ni^{2+} to another Ni^{2+} in pure NiO. The immediate result is that in a row of Ni^{2+} ions two adjacent Ni^{2+} ions are changed into Ni^{+} and Ni^{3+}. If the excess of positive charge at the Ni^{3+} ions is not sufficiently rapidly neutralized by other electrons the probability is high that the electron at the Ni^{+} ions does not travel further into the lattice, but moves back, even against the force resulting from the applied electrical field, to the original atom. The theoretical treatment of the electronic movement will obviously be quite different from that in the theory of metals and must consist of a discussion of the probability of the existence and prevalence of such charge disturbances and the chance of propagating the electrons from them to other similar disturbances. In default of such a treatment we may provisionally infer that the nature of such an electronic conduction mechanism probably implies that in a certain region the conductivity will be highly sensitive to the height of the potential barriers. Substances with partially filled energy zones will therefore, according to this qualitative picture, generally be either metals or poor conductors, whereas intermediate cases will probably be rare. Substances of the latter intermediate type, i.e. semi-conductors with appreciable conductivity, will, however, be rather interesting, since one might expect their conductivities to be very sensitive to changes in the lattice spacings and thus to the situation of the bands with respect to the potential barriers, and therefore, not only to temperature, but also to external pressure, formation of solid solutions etc.

The existence of semi-conductors or insulators with partially filled energy zones, could not, indeed, be properly understood from the viewpoint of the present theory of electronic states for metals[20, 21]. A peculiar difficulty was also offered by a substance like Fe_3O_4, for according to these views one could not immediately explain why a substance with a partially filled $3d$ band containing $5\frac{1}{2}$ electrons per Fe atom should conduct 10^{11} times as well as a substance of the same lattice type and practically identical lattice dimensions with a partially filled $3d$ band containing 5 electrons per Fe atom (γ Fe_2O_3). Similar arguments hold for the non-stoichiometric compounds. For these substances the Wilson model for extrinsic semi-conductors[4], eventually the modified model of de Boer and van Geel[22], cannot be applied. According to this theory, semiconduction has been explained by discrete impurity levels; if energy is taken up from the thermal movement, electron transitions are assumed to occur from these levels to a normally completely empty band, or from a completely filled band to empty impurity levels. In the cases under consideration, however, this mechanism cannot help us, since the energy band ($3d$) is partially filled with electrons in the stoichiometric compounds as well as in the non-stoichiometric ones; and it cannot explain the considerable increase in the conductivity if the substance no longer contains a whole number of electrons per ion.

Our consideration given above showing that substances with partially filled energy bands must actually be expected to be poor conductors, if only the potential barriers are sufficiently high to reduce the frequency of interchange below a certain limit, which, for instance, can be of the order of the inverse of the duration of an

"excited lattice state" (in our example $Ni^{+} - Ni^{3+}$), explains immediately the effect of a non-integral number of electrons per atom in a band, or, in other words, of an average structure of a cation lattice with unequally charged ions (or in part atoms) of the same element. If, for instance, in Fe_3O_4 an electron moves from a Fe^{2+} ion to a Fe^{3+} ion at an equivalent lattice point, the initial ion is transformed into Fe^{3+} and the accepting ion into Fe^{2+}. As a consequence of this reaction (indicated according to Wagner by $Fe^{2+} + Fe^{3+} \rightarrow Fe^{3+} + Fe^{2+}$), if only it occurs simultaneously at severa points in the lattice, no fundamental change in the statistical distribution of Fe^{2+} and Fe^{3+} has occurred. The essential difference from the foregoing case is that the electronic movement does not automatically imply the appearance of a charge disturbance inhibiting further electronic transport. In a perfect Fe_3O_4 crystal the chain of electronic interchanges is only broken down at the surface of the crystals. Since after each electronic transition the energy state of the lattice is not altered (except for minor effects), the amount of energy necessary for each electron transi-

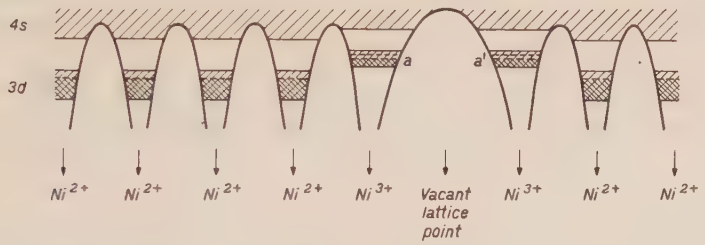

Figure 1. Schematic representation of the 3*d* and 4*s* band in a substance like NiO, containing a small amount of oxygen in excess. Section through a row of Ni^{2+} ions (110 direction) with one absent cation.

tion is very small. Such a lattice with a statistical distribution of unequally charged homonymous ions shows therefore a high conductivity and a low temperature coefficient.

Let us now consider the periodic potential field along a row of cations (in a face-centred lattice, therefore a (110) direction) in a substance with a partially filled 3*d* band like NiO, disturbed at one point by the absence of one cation (figure 1).* At absolute zero two of the only slightly broadened levels of the Ni ions adjacent to the lattice hole (in the three-dimensional lattice there are 12 such ions), *a* and *a'*, contain one electron less than the normal lattice ions. The partially filled 3*d* band of the normal lattice ions does not give rise to any appreciable conduction owing to the effect of the potential barriers, as considered above. Electronic interchange takes place easily only between the 12 cations adjacent to the lattice hole sharing 10 electrons, but this does not lead to any transport of electricity in an electric field. The 4*s* band especially is strongly broadened by the lattice, but the bands are still separated by a considerable forbidden energy region. Actually pure NiO does not absorb strongly in the region of visible light; its colour is a light yellowish green.

* Strictly speaking also the second nearest neighbours, etc. of a lattice hole have slightly raised levels, and also the potential barriers are slightly changed. The schematic picture of figures 1–3, however, is sufficient for our purpose.

The forbidden region can therefore be estimated to be somewhat less than 3 volts, Upon introduction of a small excess of oxygen, however, the colour turns into black, which is probably connected with transitions from the raised levels *a*, *a'* into the empty 4*s* zone of the lattice. The introduction of an excess of oxygen, i.e. of a number of levels *a*, *a'* (being partially Ni^{3+} ions, namely $\frac{1}{6}$ of them), simultaneously increases the conductivity, of which the mechanism can now be understood in the following way. If the temperature is above absolute zero there is a certain probability that a normal lattice Ni^{2+} ion gives off its electron to one of the Ni^{3+} ions adjacent to the lattice hole, for which transition an amount of energy must be supplied from the thermal movements in order to bring the electron into the higher levels *a*, *a'*. The result is that a row of normal lattice ions contains a Ni^{3+} ion of the same energy level as the Ni^{2+} ions, and conditions as considered for the case of Fe_3O_4 are created. Hence a chain of transitions $Ni^{2+} + Ni^{3+} \rightarrow Ni^{3+} + Ni^{2+}$ sets in, which, in the presence of an electric field, leads to electronic conduction. If during such a chain of transitions the electronic deficit propagated through the lattice meets a lattice hole, i.e. when a Ni^{2+} ion in the neighbourhood of such a hole is converted into a Ni^{3+}, there

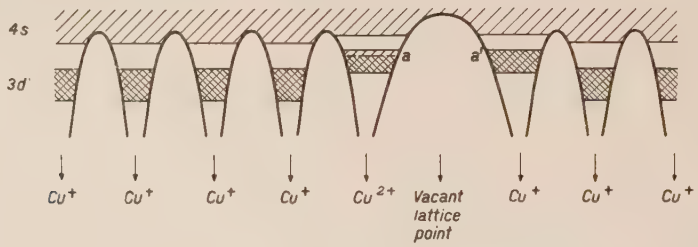

Figure 2. Schematic representation of the 3*d* and 4*s* band in a substance like Cu_2O, containing a small amount of oxygen in excess. Section through a row of Cu^+ ions with one absent cation.

is a large probability that an electron of a level *a* (*a'*) falls back to this ion, and the chain of transitions is broken down; every new chain must start again with a jump of an electron to a non-occupied level of a Ni^{3+} ion adjacent to a lattice hole. In this way an equilibrium is established, and the total number of Ni^{3+} ions at normal lattice points, and therefore the conductivity, depends on the temperature according to a Boltzmann partition law.

In the case of Cu_2O or CuJ the picture is somewhat different owing to the fact that here the band of 3*d* electrons is completely occupied. Figure 2 shows again the case of a row of Cu^+ ions and one absent cation. In this case one of the cations directly surrounding the lattice hole (in figure 2 there are only two, again represented by somewhat raised levels *a* and *a'*) contains one electron less (Cu^{2+} ion). The red colour of Cu_2O indicates that the Cu^+ 3*s* and the Cu 4*s* zone are separated by a forbidden zone of about 2 volts (the spectral photoelectric region, according to this transition, lies at about 630 mμ. corresponding to about 2 volts); the "centre" of the latter lies 12·4 volts higher than that of the former (§ 2, table 2). At absolute zero no conduction is possible, since the 3*d* band is completely occupied and the 4*s* zone is entirely empty. At higher temperature three conductivity mechanisms are possible:

(1) Electron transitions from $3d$ into $4s$.

(2) Electron transitions from levels a, a' etc. into the $4s$ zone.

(3) Electron transitions from the $3d$ band into the level a.

(1) leads to electronic movement of an electron in $4s$ and of an electron hole in $3d$, the former predominating; (2) leads only to the former, whereas electron transitions (3) imply defect conductivity in $3d$. According to measurements[18] of the Hall constant and measurements of the thermo-e.m.f.[17] of Cu_2O containing a small excess of oxygen this substance shows defect conductivity and therefore obviously the third mechanism prevails. If, however, the Cu_2O is heated in a high vacuum, the substance thus obtained, which will be now close to the stoichiometric composition, is still an electron hole conductor at lower temperatures, but above 500° it shows a negative Hall constant. Obviously the number of Cu^{2+} ions at levels a etc. is so small now that at higher temperatures mechanisms (1) and (2), owing to their larger temperature coefficient, will finally predominate over (3), whereas at lower temperatures the activation energy of (1) and (2) are too high to yield an important conductivity. It should be pointed out that the number of lattice holes of the type of figure 2 will be larger than the number of Cu^{2+} ions at such lattice holes, owing to thermal lattice deviations at the temperature at which the crystal was formed (Schottky-Fehlstellen); all such levels at lattice holes can contribute to mechanism (2), whereas only an unoccupied level a can contribute to mechanism (3). In pure Cu_2O all copper ions are Cu^{+} ions and therefore only (1) and (2) should be possible.

With increasing amount of excess oxygen ions the mutual influence of the various lattice holes and of the ions with higher charge lowers the levels a, a' etc. Owing to the statistical distribution of these lattice holes and higher charged ions the levels do not have the same height throughout, but as a whole they are all lowered more or less, since with increasing number of such vacant lattice points the direct environment of ions adjacent to the hole becomes increasingly more symmetrical and their average height above the $3d$ band is therefore lowered continually. The lowest levels give the largest contributions to mechanism (3). Actually we find that the activation energy as derived from the temperature coefficient of the conductivity of Cu_2O decreases from 0·72 volts to 0·13 volts with increasing oxygen content[23]. In the case of CuJ[24] a sufficient excess of iodine (corresponding to $Cu_{0\cdot995}J$) leads to a negative temperature coefficient, indicating that in that case the lowest levels a, a' etc. do not rise any more above the highest members of the lattice $3d$ band.

Photoconductivity occurs with Cu_2O and CuJ, not with NiO (independently of deviations from stoichiometry). With the aid of the models given above we may make the tentative hypothesis that photoconductivity, for equal relative positions of the bands with respect to the potential barriers, will be much greater in the case of figure 2 than of figure 1. This can be seen in the following way. Transitions from the lattice $3d$ band into the levels a, a' etc. need not be considered, since as optical transitions they are not allowed. Transitions (1) and (2) are permitted; both transitions can be deduced from the spectral distribution of photoconductivity in the case of Cu_2O with an excess of oxygen, a normal band with a maximum of 630 mμ. and a band connected with the oxygen excess at about 1700 mμ.[25]. In the case of a

substance with a completely filled $3d$ band a photoelectrically released electron, moving through the lattice under the influence of an applied field, for instance from a Cu^+ ion adjacent to a vacant lattice point, can only fall back to a lower level when it encounters an electronic hole. In the case of NiO, however, the wandering electron can fall back at any time to the $3d$ band, since sufficient empty electronic states are available. Also in this $3d$ band the additional electron can travel further through the lattice, until it reaches an electronic hole (Ni^{3+} ion), but in this band its mobility is considerably smaller than in the $4s$ band, owing to the higher potential barriers to be penetrated; hence only the electrons in the $4s$ band should make a practical contribution to the photoconduction. As a consequence of the much smaller average path length the photoconductivity in NiO will then be correspondingly smaller for otherwise equal conditions.

Another possibility, explaining the photoconductivity of these substances with completely filled bands, which cannot wholly be excluded, is suggested by our remark in § 2 that in CuJ the electron deficit at the lattice holes is perhaps not present

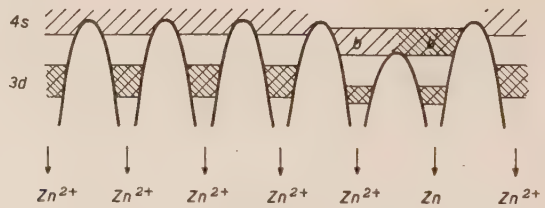

Figure 3. Schematic representation of the $3d$ and $4s$ band in a substance like ZnO, containing a small amount of Zn in excess. Section through a row of Zn^{2+} ions touching a lattice hole due to an absent oxygen ion.

at the copper ions (producing Cu^{2+}), but at the J^- ions (thus converted into J atoms). If the latter corresponds to the actual state of affairs for CuJ, the transition of an electron from the Cu^+ $3d$ band into the $5p$ level of those J atoms takes the place of transition (3), and this is permitted as an optical transition. In that case photoconduction can be explained as conduction in the Cu^+ $3d$ band as a consequence of optically released electrons according to the (modified) transition (3). This might be the mechanism for all these substances, if it could be proved to be a general rule that with cations with a complete electronic group or subgroup the electron deficit at the lattice holes is preferably located at the anions. For this a more careful calculation of the electronic levels, which must be reserved to the future, would be necessary.

For sake of completeness we also give, figure 3, the situation of the levels for ZnO containing a small amount of metal in excess, on the assumption of vacant oxygen lattice points. Electronic conduction occurs after thermal excitation of an electron from the occupied $4s$ level b' (Zn atom adjacent to a vacant oxygen lattice point) into the $4s$ band, converting a normal lattice ion into Zn^+. Photoconductivity can occur by excitation from $3d$ either into a level b, b' etc. or into the normal $4s$ band.

Finally it should be pointed out that several features of these semiconductors could be understood with the aid of a model using Smekal's structure-sensitive lattice flaws[26]. The above picture, however, enables a more complete description of the phenomena and seems preferable in the light of recent results on lattices with vacant lattice points[27,28] and on the nature of thermal lattice deviations by Wagner and Schottky.*

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* A similar treatment of the colour centres in the alkali halides has been given by de Boer[29].

DISCUSSION OF THE PAPER BY DE BOER AND VERWEY

Reported by N. F. MOTT

with the help of some notes from
R. PEIERLS

CONSIDERABLE surprise was expressed by several speakers that in crystals such as NiO in which the *d*-bands of the metal atoms were incomplete, the potential barriers between the atoms should be high enough to reduce the conductivity by such an enormous factor as 10^{10}. Mr Wilson pointed out that in that case it would hardly be correct to speak of bands at all, but one should think of sharp energy levels, as in the 4*f* shells of salts of the rare earths. This did not seem likely in view of the relatively small distance between nickel lattice points (2·9 A. compared with 2·5 A. for metallic Ni). Prof. Mott stated that in metallic nickel it is known, from experimental data on the specific heat at low temperatures, that the breadth of the *d*-band is quite large, of the order 1 eV.

Prof. Peierls agreed with Dr de Boer that the existence of semi-conductors with incomplete *d*-bands could not be understood merely by considering the low transparency of the potential barrier. This transparency could be perhaps 10^{-2} or 10^{-3} less than for ordinary metal but not 10^{-10}. He suggested that a rather drastic modification of the present electron theory of metals would be necessary in order to take these facts into account. The solution of the problem would probably be as follows: if the transparency of the potential barriers is low, it is quite possible that the electrostatic interaction between the electrons prevents them from moving at all. At low temperatures the majority of the electrons are in their proper places in the ions. The minority which have happened to cross the potential barrier find therefore all the other atoms occupied, and in order to get through the lattice have to spend a long time in ions already occupied by other electrons. This needs a considerable addition of energy and so is extremely improbable at low temperatures.

It appears, therefore, that if the transparency is at all small, the electrostatic interaction would reduce the conductivity still further and thus that at low temperatures the conductivity is proportional to a high power of the initial transparency. No mathematical development of these ideas has however yet been given.

Prof. Peierls made some further remarks about semi-conductors containing impurities. Suppose the impurity is capable of giving off an electron; it is then not sufficient to remove the electron into one of the adjoining lattice ions, in order to make it free for electronic conduction. This is because the impurity is then left in an ionized state and will attract the electron, which therefore moves in the periodic

field of the lattice with a Coulomb field superimposed. It is known that in such a field the electron is capable of discrete bound states of negative energy (as in the field of a positive ion). Only if the energy of the electron is still further increased so that it can overcome this attraction and move right away from the impurity centre will it become a conduction electron in the proper sense. This suggests that, even if, as might conceivably happen, an electron would *gain* energy in moving from the impurity atom to an adjacent lattice ion, nevertheless the lowest state of the electron would *always* be a bound state in the neighbourhood of the impurity centre, in which it, so to speak, revolves round the centre, even though it is not definitely attached. Hence a finite activation energy should always be necessary to produce conduction electrons. This conclusion no longer holds when the number of impurity centres becomes large* because then the electron need not overcome the attraction of its "home" centre completely; already at a small distance from it, it will come under the simultaneous attraction of other centres and will thus be released.

From these arguments one may draw the conclusion that one should never find a substance in which a *small* concentration of impurity can produce a conductivity *without* activation energy.

It may be possible to explain on these lines the dependence of activation energy on concentration shown by most semi-conductors.

Similarly it should be true that pure substances of stoichiometric composition should never show a very small number of conduction electrons with zero activation energy. In this connexion it is perhaps significant that one metal with a very small number of conduction electrons, bismuth, shows a correspondingly small effective electron mass. A small mass means a large radius of the orbit and hence the minimum distance at which the centres will interact is correspondingly increased.

Prof. Pohl called the attention of the conference to the behaviour of AgBr, which at room temperature shows electrolytic conductivity, but which is normally an insulator at low temperatures. If it is irradiated with 10^{12} quanta per cm^3 it shows electronic conductivity like a semi-conductor. The state is destroyed by high temperatures and high fields.

* I.e. comparable with number of atoms in the lattice.

PART II

CONDUCTION IN ALLOYS

RESISTANCE OF ALLOYS WITH DISORDERED AND ORDERED ARRANGEMENT OF ATOMS

By G. BORELIUS (Stockholm)

§ 1. RESISTANCE CONCENTRATION DIAGRAMS

The general features of the resistance of alloys in the simplest cases is illustrated by the behaviour of the series of binary alloys of gold with silver, copper and platinum shown in figure 1. The simple bent curves in the {resistance, concentration} diagrams, as we now know, belong to homogeneous alloys with a disordered arrangement of the atoms at the lattice points. In the systems Au-Ag this type of curve is obtained whatever the rate of cooling. In the systems Au-Cu and Au-Pt the homogeneous disordered state is stable only at high temperatures and can be preserved at room temperature only by quenching. With slow cooling, ordered states appear in the Au-Cu system with maxima of order and sharp minima of resistance at simple values of the concentration (Cu_3Au and CuAu). In the Au-Pt system the solubility is limited at temperatures below 1150° C., and the resistance curves obtained after quenching from different temperatures are approximately straight lines in the region where two phases co-exist.

Ordered arrangement of atoms (superlattices), and the presence of more than one phase, are thus often very well marked in resistance diagrams. In earlier days most metallographers had very little confidence in resistance measurements as a method in metallography. As the laws of resistance of alloys are now better known, and particularly owing to the increased significance of superlattice formation and segregation processes, the resistance measurements have nowadays an importance in metallography comparable with investigations by microscopes, X rays and thermal analysis. Whereas resistance measurements in recent years have been used by Grube[4] and others for extensive investigations of various complicated systems of alloys, our measurements have been mainly directed to the study of the resistance and the phenomena influencing the resistance from a physical point of view, and we have in the first place sought out the simplest systems showing the various phenomena.

In the following, §§ 2 and 3 will deal with measurements of disordered homogeneous alloys, §§ 4 to 9 with superlattices, and § 10 with the segregation process.

§ 2. RESISTANCE OF DILUTE SOLID SOLUTIONS OF *b* METALS IN COPPER, SILVER AND GOLD

The shape of the {resistance, concentration} curves of homogeneous alloys without superlattices is above all influenced by the slopes at the sides near the pure metals. It is usual to characterize this slope by the increase ζ in the resistance caused by the addition of one atomic per cent to the pure metal.

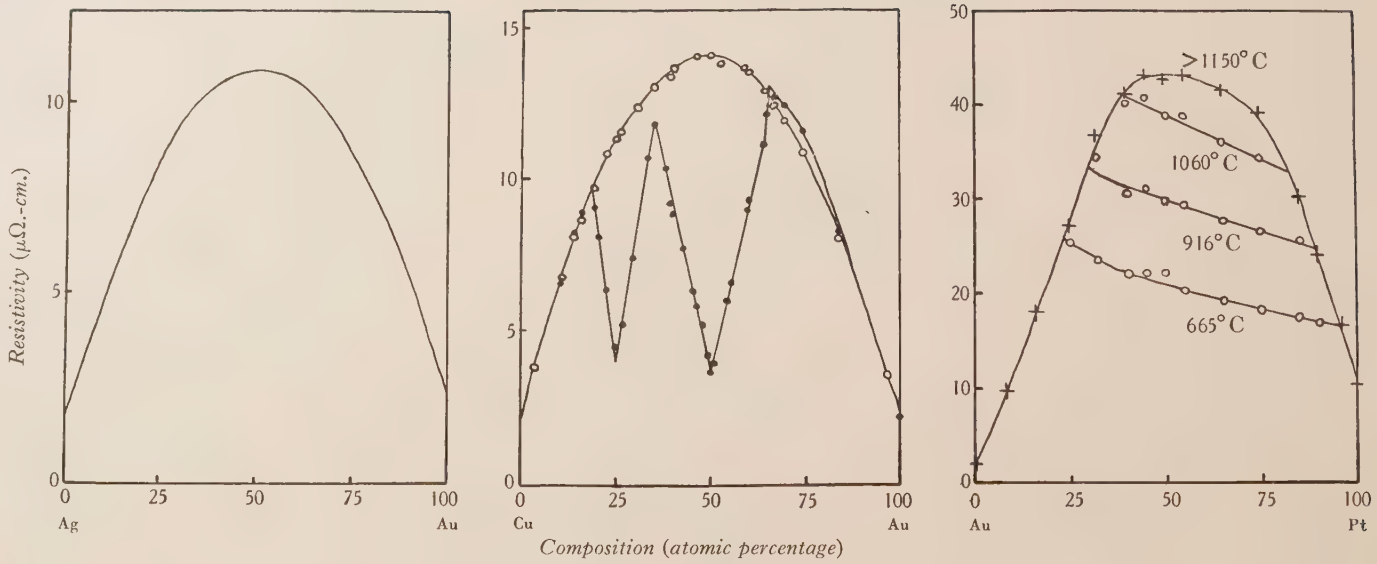

Figure 1. {Resistance, concentration} diagrams for room-temperature. (*a*) Silver-gold alloys according to measurements of Matthiessen[1]. (*b*) Copper-gold alloys according to Johansson and Linde[2]. (*c*) Gold-platinum alloys according to Johansson and Linde[3].

It was first pointed out by Benedicks[5] in a paper published in the Swedish language that the additional resistance often increases with the distance in the periodic system between the dissolved metal and the solvent. Better known is the work of Norbury[6], who found the horizontal distance in the long-periodic system to be of decisive importance.

Linde[7] has made a very extensive investigation of the increase in resistance of the metals Cu, Ag and Au of the 11th group of the periodic system due to the addition of various metals. The results are especially simple in the case of addition of *b* metals, that is metals from the groups 12 to 15. Figure 2 shows his results from published and unpublished measurements. The square of the difference of group numbers of dissolved metal and solvent is taken as abscissa in these diagrams. The metals of each period give nearly a straight line.

Linde[7] has also pointed out another interesting feature of these additional resistances. They are nearly the same if a certain *b* metal is added to Au or Ag; but on an average only 80 per cent of these values if the same metal is added to Cu. He relates this observation to the fact that the atomic volumes of Au and Ag are 10·3 and 10·2 respectively, whereas the atomic volume of Cu is only 7·1. From this he became interested in the influence of compression on the additional resistance ζ, and he has during recent years obtained a great number of measurements on this subject which are not yet published. The change of resistance of the dilute alloys, measured at pressures up to 3000 kgf./cm^2, is first corrected for the change of volume so as to give the change of specific resistance ρ. Figure 3 shows these changes reduced to 1 kgf./cm^2 for some systems as a function of concentration. The effect of pressure $d\rho/dp$ always gets more negative by addition of *b* metals. This decrease of $d\rho/dp$ for one atomic per cent, divided by the additional resistance ζ per cent, i.e. the quantity $\zeta^{-1} d\zeta/dp$, may be looked upon as a pressure coefficient of the additional resistance. As appears from table 1, this quantity is of the same magnitude as the compressibility $V^{-1} dV/dp$, as would be expected if the additional resistance contained the atomic volume V as a power not too far from the first as a factor.

Table 1. Pressure coefficients of additional resistance ζ for one atomic per cent of *b* metals in Cu, Ag and Au compared with the coefficient of compressibility of the pure metals. Unpublished measurements by Linde

	Added metals	Copper	Silver	Gold
$\frac{1}{V}\frac{dV}{dp}\cdot 10^6$	—	−0·72	−0·99	−0·58
$\frac{1}{\zeta}\frac{d\zeta}{dp}\cdot 10^6$	Al	−0·4	—	—
	Ga	—	−1·18	−0·68
	Ge	−0·60	—	—
	Sn	−0·66	—	—
	As	−0·45	−0·33	—
	Sb	−0·69	—	—

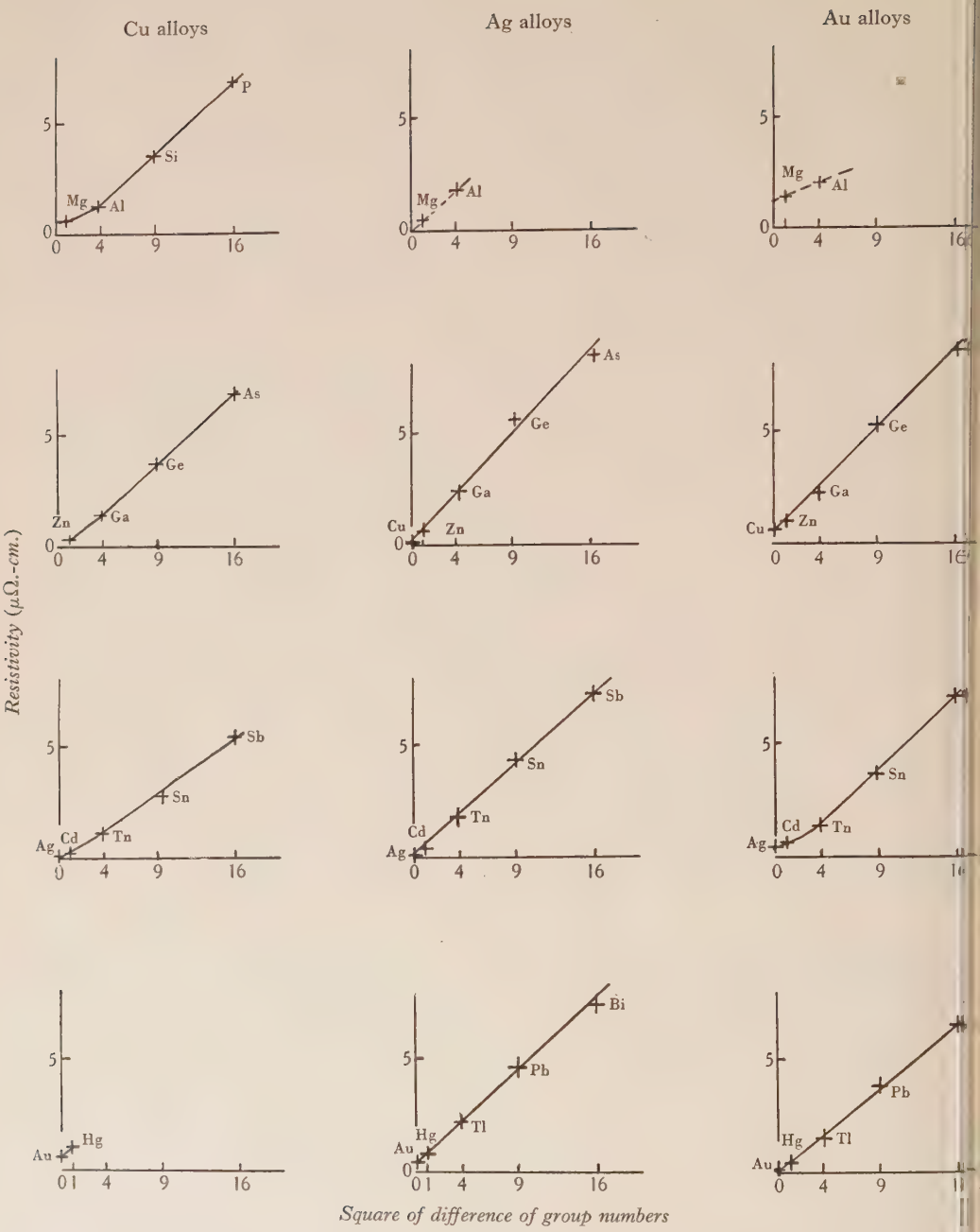

Figure 2. Increase in resistance for 1 atomic per cent of various *b* metals added to copper, silver and gold. (Measurements by Linde.)

For this group of alloys the rule of Matthiessen is also approximately valid. This rule predicts that if the specific resistance ρ of an alloy is written

$$\rho = \rho_0 + \rho_T \qquad \ldots\ldots(1),$$

where ρ_0 is the resistance at the absolute zero and ρ_T thus the thermal electric resistance, the addition of foreign atoms to a pure metal increases ρ_0 but has very little influence on ρ_T. In fact Linde has found $d\rho/dT$ to increase slowly with increasing ρ for the dilute alloys of copper, silver and gold with the *b* metals.

The disordered homogeneous alloys of Cu, Ag and Au with each other and with the other *b* metals thus are especially simple in their electric behaviour and have been the first object for theoretical treatment. In the classical electron theory,

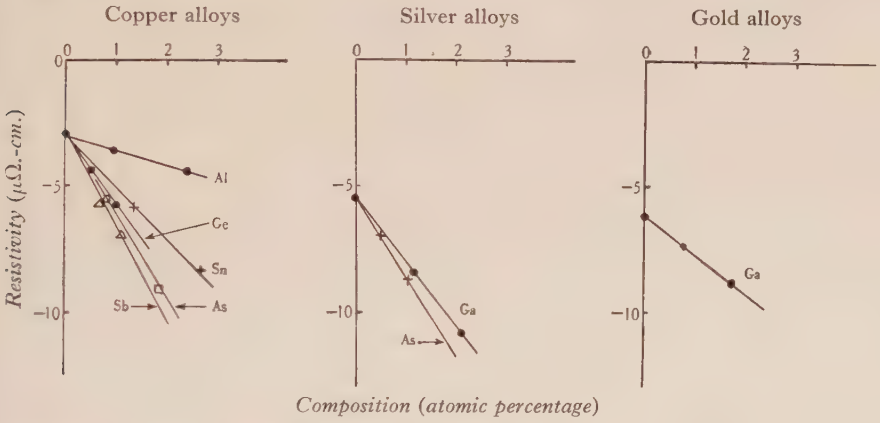

Figure 3. Change of specific resistance for 1 kgf./cm² due to the addition of *b* metals to copper, silver and gold. (Unpublished measurements by Linde.)

insuperable difficulties arose already in connexion with the Matthiessen rule. In the general expression for the specific resistance

$$\rho = \frac{2m}{e^2}\frac{v}{nl} \qquad \ldots\ldots(2),$$

where m and e denote mass and charge of an electron, the mean velocity v was found to be proportional to the square root of the absolute temperature T, and the variation of the number n of electrons per cm³ and their mean free path l could not possibly be accounted for in such a way as to give the Matthiessen formula. The modern theory assumes v to be large and, to a first approximation, independent of temperature; and the variations of ρ with temperature are mainly due to the variations of l. Now $1/l$ is a measure of the scattering of the conducting electrons, and this scattering is a sum of one part, due to thermal agitation, and one due to the disordered arrangement of the foreign atoms.* The scattering of the conducting electrons was first

* It might be worth mentioning that this general description of the Matthiessen rule was already given by Höjendahl[8] some years before the appearance of the Sommerfeld theory on the basis of ideas put forward long ago by Wien[9]. Though the theory of Höjendahl is now superceded, it should be remembered for its good services in those years when the problems concerning superlattices were first approached. When the Sommerfeld theory appeared[10] it was at once evident and pointed out[11] that this theory was of the general type which could explain the main features of conduction in alloys.

discussed by Bloch[12], who showed that there should be no scattering in a perfect periodic lattice, and the scattering in alloys has been discussed from the standpoint of wave mechanics especially by Nordheim[13] and Mott[14, 15]. Mott has managed to give an explanation of the variations of the additional resistance with the group number of the dissolved metal by taking into account the scattering power of the extra field due to the charges of the foreign atoms, those charges being proportional to the differences of the group numbers of the dissolved metal and the solvent.

The pressure dependence of the resistance of dilute alloys has been treated theoretically by Lenssen and Michels[16] and Mott[17]. Their results, however, do not seem to be in direct agreement with the experimental results of Linde. A re-examination of the assumptions underlying the calculations, with the guidance of the empirical results, might therefore be of interest.

§ 3. RESISTANCE OF SOLID SOLUTIONS OF TRANSITION METALS IN COPPER, SILVER AND GOLD

As shown definitely by the measurements of Linde, the simple rules valid for the alloys of the monovalent metals Cu, Ag and Au with the *b* metals cannot be extended to their alloys with the *a* metals (or transition elements). As an illustration of Linde's results, figure 4 gives the specific resistance ρ at 0° C., the dependence on temperature $d\rho/dT$, and the pressure dependence $d\rho/dp$ for alloys of Au with the transition metals of the first long period plotted against the atomic concentration. We see from figure 4*a* that the increase in resistance for one atomic per cent does not follow the order of the atomic numbers (Ni, Co, Fe, Mn, Cr, Ti); from figure 4*b* we see that the Matthiessen rule which predicts that $d\rho/dT$ should increase slowly with concentration does not hold for these alloys; and from figure 4*c* that the pressure coefficient is of variable size and in most cases positive (it was negative for the alloys with the *b* elements). For Co, Mn and Cr, $(d\zeta/dp)/\zeta$ has the values $-0{\cdot}2$, $+1{\cdot}3$ and $+1{\cdot}1 \times 10^{-6}$ respectively.

In fact, the transition metals influence the resistance of the monovalent metals in a rather individual and varying way, and these variations are of great practical importance in discovering alloys suitable for resistance materials and for pressure measurements. Linde's results have given rise to various new ideas in these directions.

The peculiar influence of the transition metals on the resistance is obviously connected with their strong paramagnetic or ferromagnetic properties. For information about the electric behaviour of these alloys, it is therefore also a matter of importance to study their magnetic properties. In our laboratory Gustafsson[18] is now investigating the paramagnetism of alloys of Cu, Ag and Au with transition metals at temperatures ranging from room temperature to 450° C. The measurements at present include dilute alloys of Cu, Ag and Au with Mn and the systems CuNi and AgPd. His results suggest that a considerable amount of experimental work will be necessary before the paramagnetic alloys are sufficiently classified even from a purely phenomenological point of view. Nevertheless the theory regarding

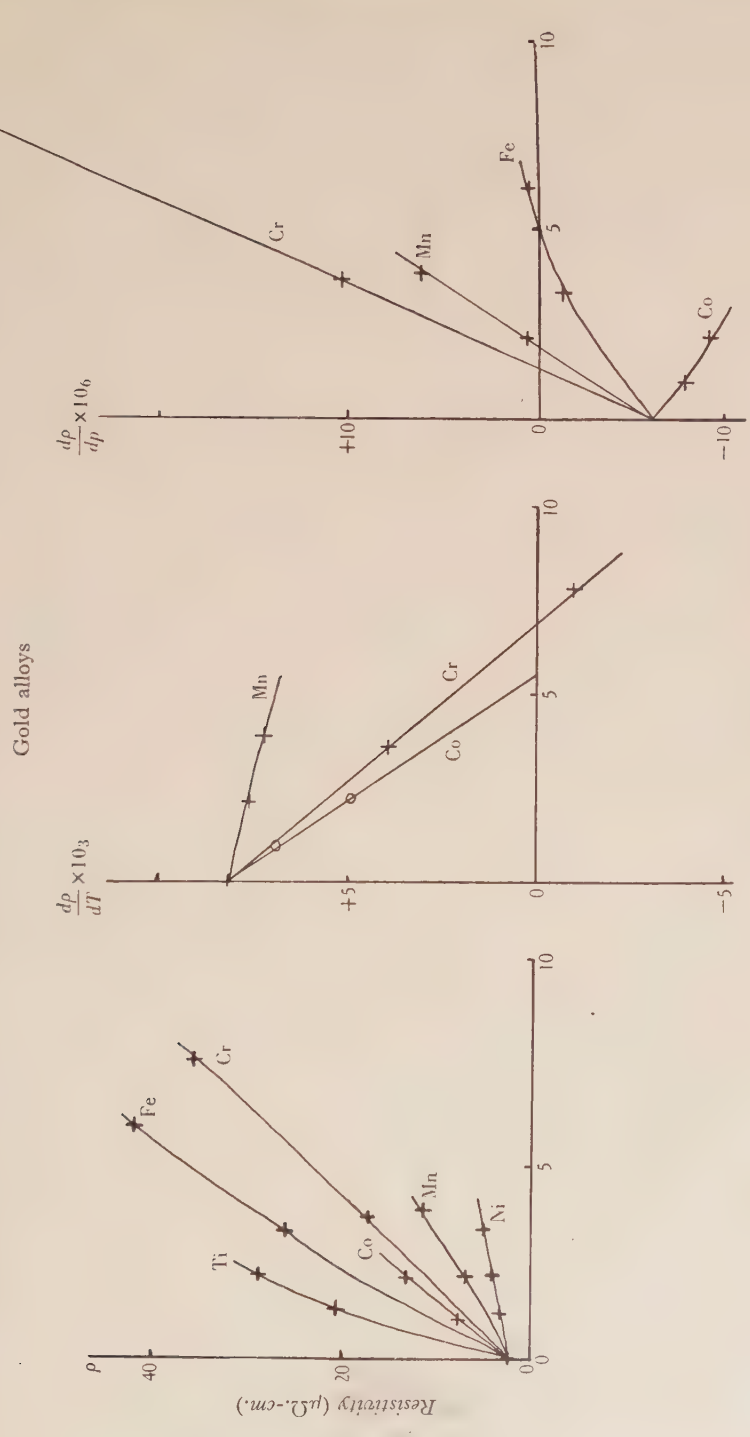

Figure 4. Specific resistance and its dependence on temperature and pressure for dilute alloys of Au with *a* metals. (Measurements by Linde.)

the exchange of electrons between the unfilled electron bands of the transition metals has proceeded through the works of Stoner[19], Slater[20], Mott[21] and others to a qualitative understanding of various types of paramagnetic phenomena. Indeed, it seems as if the theory is in advance of the experiments and highly in need of the guidance of further experimental work for its definite stabilization.

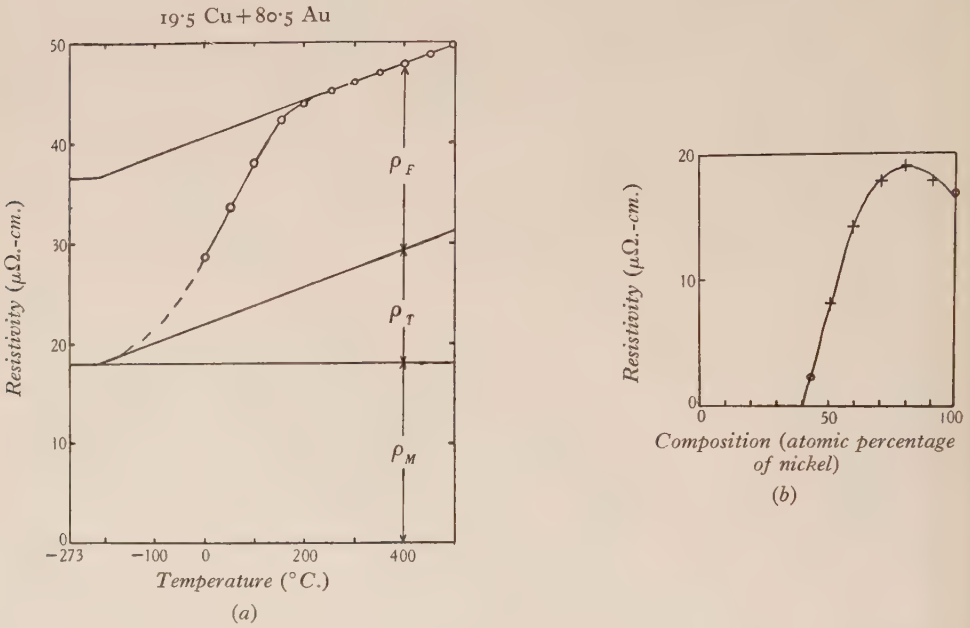

Figure 5. (*a*) Resistance of a ferromagnetic CuNi alloy. (*b*) Ferromagnetic part of resistance of CuNi alloys. (Measurements by Svensson[24].)

Experimentally better known are the relations between resistance and ferromagnetic properties, which both have been extensively studied in the system CuNi. The resistance of these alloys has been measured by Chevenard[22], Krupkowski and de Haas[23] and Svensson[24]. As is shown in figure 5*a* taken from the paper of Svensson, the resistance of a ferromagnetic alloy can be described phenomenologically as a sum of one part ρ_M due to the mixed arrangement of the Cu and Ni atoms, one normal thermal part ρ_T due to the thermal agitation of atoms, and one magnetic part ρ_F increasing from 0 to its maximal value with increasing demagnetization. The dependence on concentration of the maximum values of ρ_F is shown in figure 5*b*.

§ 4. DEVELOPMENT OF TRANSFORMATIONS FROM DISORDERED TO ORDERED ATOMIC ARRANGEMENTS

The question of the ordered or disordered arrangement of the two kinds of atoms at the lattice points of a binary alloy was first discussed in detail by Tammann[25], his starting point being results from chemical investigations. He found that there existed certain concentration limits for the resistivity to the chemical

action of agencies which attack only one of the components of the alloy. Thus, for example, there were limits at 50 per cent Au for the action of nitric acid on CuAu and AgAu alloys. To explain these limits Tammann found it necessary to assume an ordered arrangement of the atoms and predicted these arrangements from a principle of "best possible mixing" (*bestmögliche Durchmischung*).

This hypothesis led to several X-ray investigations of alloys. Vegard[26] and von Laue[27] had pointed out that an ordered arrangement should give rise to certain extra lines. On the one hand the search for such extra lines in several systems, among them also systems such as AgAu, where Tammann had found sharp chemical resistivity limits, gave negative results; on the other hand, Bain[28] on Cu_3Au and Phragmén[29] on Fe_3Si found extra lines, which were looked upon as support for the hypothesis of Tammann. As at that time there was some uncertainty as to the evidence of X-ray results in the case of incomplete order, it was somewhat difficult to draw the right conclusions from these investigations; also the conclusions drawn from the chemical work were found to be very uncertain[30,31].

My collaborators and I approached the problem from thermoelectric and conductivity measurements carried out especially by Sedström[32] for a number of alloy systems. We found it most likely that the smooth resistance-concentration curves obtained for these properties in most systems of solid solution indicated a disordered arrangement of atoms, whereas the sharp minima in the cases of compounds were due to ordered structures. With this hypothesis X-ray examinations were started with the results of the resistance measurements as a guide. The examination of the systems PdCu and PdAu by Holgersson and Sedström[33] gave some support to this hypothesis and later full evidence was obtained from the examination of the systems CuAu, CuPd and CuPt by Johansson and Linde[34]. In the CuAu system the compounds Cu_3Au and CuAu formed by slow cooling of the solid solutions somewhat below 400° C. were known to exist from an investigation by Kurnakow, Zemczuzny and Zasedatelev[35]. Johansson and Linde[34] found that alloys of this system quenched from above 400° C., giving high resistance values on the smooth curve in figure 1*b* first observed by Matthiessen, only gave the ordinary X-ray interferences due to the face-centred cubic lattice, whereas the alloys with concentrations in the neighbourhood of 25 and 50 per cent Au, which were tempered below 400° C. to get small resistance values, showed extra interferences indicating ordered arrangement of the two kinds of atoms on the lattice points. These extra interferences appeared not only at exactly 25 and 50 per cent, but on both sides of these concentration points in wide ranges, at the boundary of which the degree of order could only be a very moderate one. Similar results were obtained for the systems CuPd and CuPt.

These investigations thus showed that the X-ray methods were capable of detecting even a very incomplete order, that a highly disordered arrangement of atoms was, especially at high temperatures, a very frequent case in solid solutions, and that the ordered arrangement appeared only at certain limited ranges of concentration and temperature.

These results have been confirmed and extended by a great many investigations

in subsequent years. Theoretical discussions have been especially stimulated by the investigations of the CuAu alloys, for which a recent list of references[2] embraces more than 50 papers, and by the investigations of Bradley and Jay[36] of the FeAl alloys.

§ 5. CONTINUOUS VARIATIONS OF DEGREE OF ORDER

The transformations of alloys from disordered to ordered states differed from the well-known transformations of pure metals and salts into new modifications in so far as it was, for the ordering process, possible to imagine a continuous row of intermediate states between full disorder and full order. It was thus possible that the transformations might proceed wholly or in part homogeneously.

To prove this we followed the transformations by resistance measurements[37] and concluded from the results that the transformation was at least in part continuous. The {resistivity, temperature} diagrams obtained for a highly ordered alloy by increasing the temperature had the general appearance shown in figure 6. The straight lines from a to b and from e to f apply to the ordered and the disordered

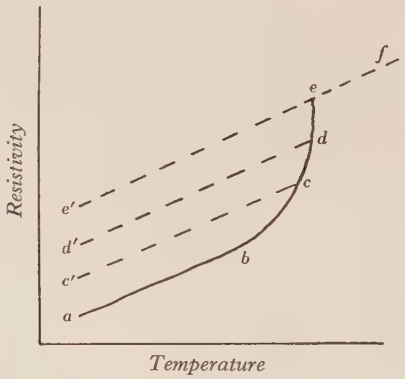

Figure 6. Schematic {resistivity, temperature} diagram of an alloy with superlattice transitions.

states respectively. In both cases the slope $d\rho/dT$ is approximately that calculated from the Matthiessen rule written in the form

$$\frac{d\rho}{dT}=p\left(\frac{d\rho}{dT}\right)_1+q\left(\frac{d\rho}{dT}\right)_2 \qquad \ldots\ldots(3),$$

where $(d\rho/dT)_1$ and $(d\rho/dT)_2$ are the slopes for the pure metals and p and q their fractional parts in the alloy. The curved part of the diagram from b to d with unusually large values of $d\rho/dT$, represents the continuous variation of structure. That changes of state really occur from b to c and from c to d may be proved by quenching the alloy from b, c and d respectively to room temperature. The remaining resistance differences ac' and $c'd'$ show that a change of state has really taken place. In fact, so far as our present knowledge reaches, values of $d\rho/dT$ much greater than those calculated from the Matthiessen rule always indicate some change either of the magnetic or the structural state. Gorsky[38] at the same time by an X-ray examination

of the tetragonality of the AuCu alloy also made the existence of a continuous transformation probable, and, independently of ours, resistivity measurements were carried out by Grube and Weber[38a].

§ 6. DEFINITIONS OF DEGREE OF DISORDER

A homogeneous solid solution with completely disordered arrangement of the atoms, or a compound with complete order is thermodynamically wholly described by its concentration q, its temperature T, and its pressure p. For the thermodynamical treatment of homogeneous solutions with incomplete order we also need a measure, ξ say, of the degree of disorder. As long as only the thermodynamically stable states are considered, ξ is determined by the values of q, T and p. However, the experimental study of the superlattices shows that frozen and unstable states are easily obtainable as well as the stable ones, and that they are often of the same practical and theoretical importance as the latter. These frozen or unstable states and their measurable physical properties such as energy, entropy, free energy, lattice constants, and resistance, are functions not only of q, T and p but also of ξ as a new independent variable.

Here, in fact, a very great difficulty arises in finding a measure of the degree of disorder that may be both theoretically defined without uncertain assumptions and also put in relation to the various physical properties used for the experimental study of the transition phenomena. The attempts made hitherto to define a suitable degree of disorder (or of order) group themselves along three different theoretical lines.

The first line starts from a discussion of the arrangement of the neighbouring atoms, the discussion having hitherto been limited to the consideration of pairs of atoms. To give an example of the theoretical treatment we may take an alloy of the composition A_3B with a superlattice of the sort found in Cu_3Pd and Cu_3Au. Then in the ordered state a fraction $f_0 = 1/2$ of all pairs of nearest neighbours are of the type AB, and by the disordering process this fraction is decreased to $f_d = 3/8$. A state of incomplete order may therefore be described by the fraction f or better by a degree of disorder

$$\delta = \frac{f_0 - f}{f_0 - f_d} \qquad \ldots\ldots(4),$$

ranging from 0 to 1, or by a degree of order $\sigma = 1 - \delta$. My collaborators and I[37] discussed already in 1928 this way of finding a formal description of the transition phenomena though, for reasons mentioned below, we did not find it very suitable. In recent years, however, Bethe[39] and Peierls[40] have made an extended use of an "order of neighbours" σ, which may be identified with the σ above. Their use of this σ is based on the assumption that the energy of transformation should be proportional to it. I cannot find, however, that there is very much physical support for this assumption; the results of specific heat measurements by Sykes and Jones[41] do not support it. Furthermore the simple use of measures of disorder based on the arrangement of pairs of neighbouring atoms seems to be limited to transitions where the number of nearest neighbours is not altered by the transition

process. The 50-per-cent alloys CuPd, CuAu and CuPt in the disordered state are all face-centred with 12 nearest neighbours to each atom, whereas in the ordered state CuPd is body-centred with 8 neighbours, CuAu tetragonal with 8 nearest neighbours and 4 at a somewhat greater distance, and CuPt trigonal with 6 atoms nearest and 6 a little more distant from each atom. Here the use of σ is thus already precluded for purely formal reasons.

The second line starts from the state of full order. If we take as example a 50-per-cent alloy AB, this alloy can be described as a combination of two similar lattices, one containing A atoms, the other B atoms. The fraction p of B atoms in the A lattice (or A atoms in the B lattice) varies from 0 to $\frac{1}{2}$ as the alloy goes from the ordered to the disordered state, and $\alpha = 2p$ or $4p(1-p)$, etc., are possible measures of the degree of disorder ranging from 0 to 1. To make such measures quite definite, however, it is necessary to assume the distribution of A and B atoms within each lattice to be statistically disordered, and the truth of this assumption is not quite evident as there might for example be a tendency of the atoms to occur in pairs or small groups in the wrong lattice. Further, it is of course unsatisfactory to extend the idea of different A and B lattices also to the case of great disorder.

A measure of degree of disorder of this kind (called *Fehlordnungsgrad*) was first used by Wagner and Schottky[42] and related to the variations of energy, entropy and resistance in small deviations from full order. Ölander[43] later used it for the theoretical discussion of results of measurements of electrode potentials of alloys at high temperatures. The author[44] made an extended use of a measure of this type for a quantitative treatment of the transition in AuCu. Bragg and Williams[45] used a degree of order of this kind for the treatment of transitions in alloys of the type AB or A_3B and the "long-distance order" of Bethe[39] belongs to the same group of parameters.

In a discussion of the general features of the equilibrium diagrams of systems with superlattices, the author[46] has tried a third line, avoiding parameters based on description of atomic arrangements, and using a purely thermodynamical quantity, the zero-point entropy S_0, as a measure of degree of disorder. For this limited purpose, this parameter is a very suitable one. If the zero-point energy is given as a function of S_0 and the concentration q, certain boundary lines of the equilibrium diagram can be constructed in a simple way. It has not, however, yet been shown whether a quantity like S_0 can be useful also for the treatment of physical properties such as the resistance. This will depend upon whether there exists and can be found some direct theoretical connexion, for instance between zero-point resistance and zero-point entropy.

§ 7. ANTIPHASE REGIONS IN PARTLY ORDERED CRYSTALS

The proposed parameters of degree of disorder are of course single-valued only for homogeneous alloy phases and can only be used for the treatment of states of equilibrium of homogeneous frozen states obtained by quenching, and of the homogeneous metastable states which will be discussed in the next paragraph. As soon,

however, as the transitions from disordered to ordered states were followed with X-ray and resistance measurements, my collaborators and I[37] found reasons also for the existence of more complicated transitional states neither fully homogeneous nor in the ordinary sense heterogeneous. If the ordering process starts at, and spreads from, a great many points, the nuclei thus formed will as they meet coalesce if they are in phase with each other, or exist side by side as antiphase regions if they are not. This means that a row or plane of *A* atoms in one region will, as is shown in figure 7 taken from our paper of 1928[37], continue as a row or plane of *B* atoms in the next one.

It was pointed out in this paper that such regions, if they were small enough, must have a great influence on the sharpness of the superlattice lines of X-ray photograms and on the resistance.

This hypothesis of antiphase regions also explains the observation later made by Oshima and Sachs[47] and by Dehlinger and Graf[48] by X-ray examination of single

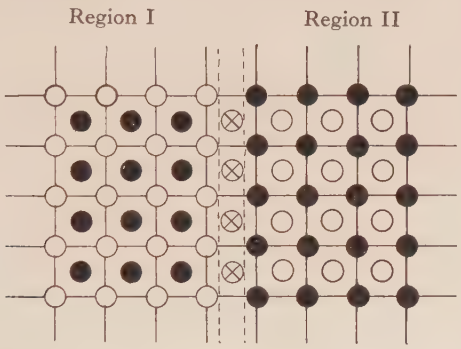

Figure 7. Antiphase regions. ○ *A* atoms, ● *B* atoms, ⊗ *A* or *B* atoms.

crystals of AuCu, that the tetragonality and the intensities of different superstructure lines do not vary in the same way during the ordering transition. The hypothesis put forth by Oshima and Sachs and especially used by Dehlinger[49] to account for these observations, namely that the tetragonality to a certain extent should be independent of the degree of order, is quite incomprehensible and, at least for the present, unnecessary.

In recent years the hypothesis of antiphase regions has indeed obtained very good support in two different ways.

On the one hand Sykes in collaboration with Evans[50] and Jones[41] has made a thorough experimental examination of the transitions in Cu_3Au by measuring lattice constants and intensity of superstructure lines, resistance, and specific heat, and has found it possible to account for a great many details, some even quantitatively, from the assumption of antiphase regions. Figure 8 shows in a schematic way some of their results concerning resistance and energy content, which are interpreted in the following way: As a sample is quenched from above the critical temperature T_0 it remains in the disordered state and resistance and energy varies along the straight lines *a*–*a*. As the quenched alloy is heated at a rate of about 90° per hour, as shown

by the curve *b–b*, the energy begins already at 60° C. to deviate from this line. This decrease in energy content is interpreted as due to the formation of small antiphase regions of an extent of only 6 to 8 atomic diameters. At about 250° C. a new decrease of energy begins owing to an increase of the size of the antiphase regions. At 344° C. this size is about 12 to 14 diameters, being estimated both from the breadth of the superlattice lines and from the energy content. The resistance is not appreciably influenced by the small regions of 6 to 8 diameters but decreases rapidly

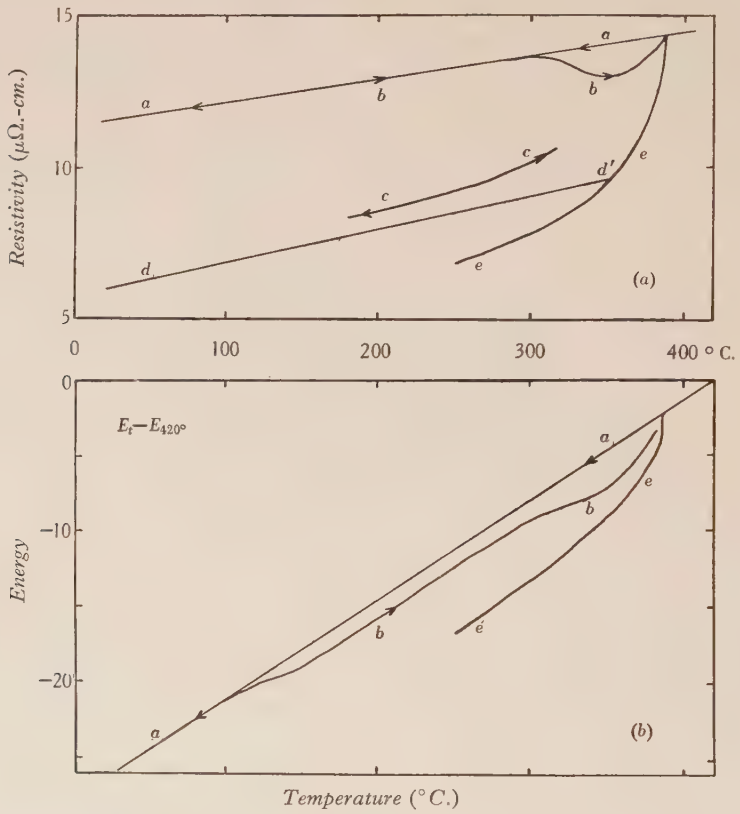

Figure 8. (*a*) Resistivity, (*b*) energy of Cu_3Au. (Measurements by Sykes, Evans and Jones[41, 50].)

as the length of the regions exceeds about 10 diameters. This is in qualitative agreement with the fact that the mean free path of the electrons in the ordered alloy is estimated, from modern theory of conduction, at 30 to 40 diameters. The curves *e–e* reached by very slow cooling correspond to regions of about 100 diameters or more and are approximately curves of equilibrium. If an alloy, which is in equilibrium at the point *d'* and thus has large antiphase regions but an incomplete order of atoms, is cooled rapidly enough to preserve the degree of disorder, the resistance follows a straight line *d–d'*. The curve *c–c* finally shows the variation of resistance by slow heating or cooling of a sample with regions of medium size in a temperature

range where the regions cannot grow. The bend is due to the variation of degree of disorder inside the regions.

On the other hand Johansson and Linde[2] have found that alloys with compositions around CuAu after suitable heat treatment occur in an ordered state (CuAu II) that can be described as the well-known ordered tetragonal state (CuAu I) found earlier by the same authors split up in antiphase regions of a fixed length. This structure, being periodic, can be directly established by X-ray examinations. At 50 per cent Au the length of each region is, as shown in figure 9, 10 atomic distances, but it increases at both sides in the concentration diagram. As to the theory of electric resistance, it is interesting to notice that these periodic antiphase displacements do not, like the accidental ones of the same mean distances, increase the resistance. Alloys with the structures CuAu I and CuAu II lie in figure 1*b* on the same resistance curve.

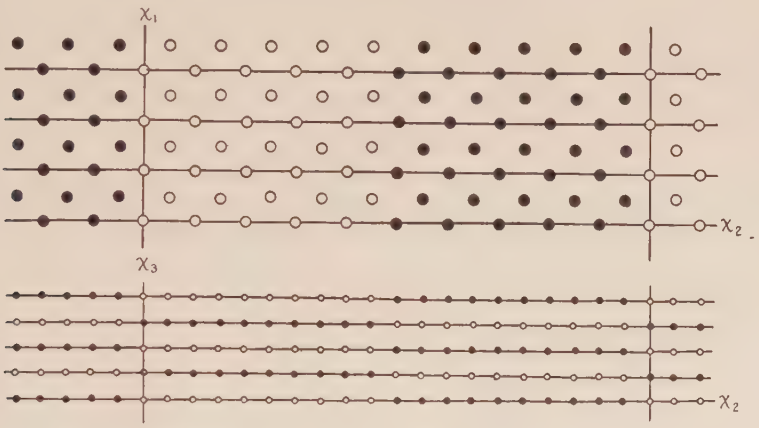

Figure 9. Structure of CuAu II according to Johansson and Linde[2].

§ 8. DISORDERING BY MECHANICAL TREATMENT

The superstructure of an alloy can be destroyed not only by heating but also by cold working. This was made probable by X-ray investigations of Dehlinger and Graf[48] on CuAu and of Schäfer[51] on FeAl and is shown very convincingly by Dahl[52] by X-ray investigations together with resistance measurements on Cu_3Au. Fig. 10*a* shows the increase in resistance for an annealed Cu_3Au alloy as a function of the decrease of section area by cold workings. Figures 10*b* and 10*c* show corresponding curves for two Cu-Pt alloys obtained by Linde in connexion with an unpublished re-examination of the CuPt system. This effect might be explained by the formation of antiphase regions by the cold working.

§ 9. HYSTERESIS BETWEEN THE ORDERING AND DISORDERING TRANSITIONS

As the transitions between ordered and disordered states were first followed in both directions by resistance measurements, in many cases a well-marked hysteresis loop in the {resistivity, temperature} diagram was found. Figure 11 gives two

examples from our first investigation[37], showing the behaviour of quenched alloys during slow heating and subsequent slow cooling. In heating an ordering process is observed to begin at the temperatures marked as T_1 and by further heating full disorder is reached at the temperatures T_3. In the subsequent cooling the alloy remains in the disordered state far below T_3 until about a temperature T_2 when the speed of the ordering process increases rapidly within a range of a few degrees. The disordered alloy could be held for many hours at temperatures between T_3 and T_2.

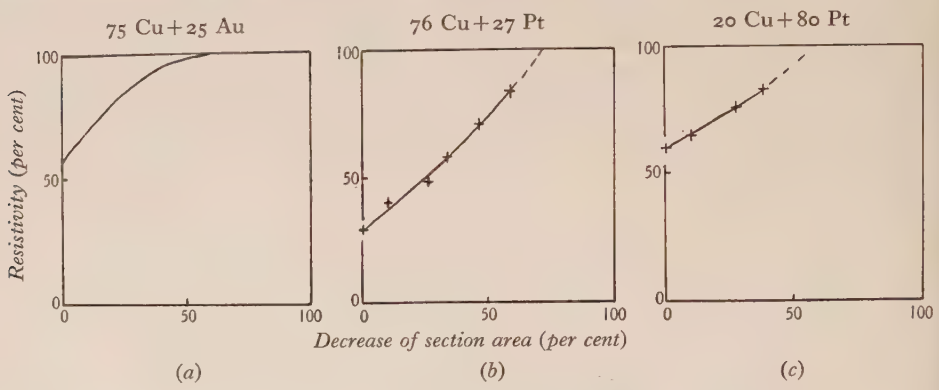

Figure 10. Increase of resistance by cold-working of alloys with super-structures. Resistance as a percentage of the resistance of the disordered state. (Unpublished measurements by Dahl[52] and Linde.)

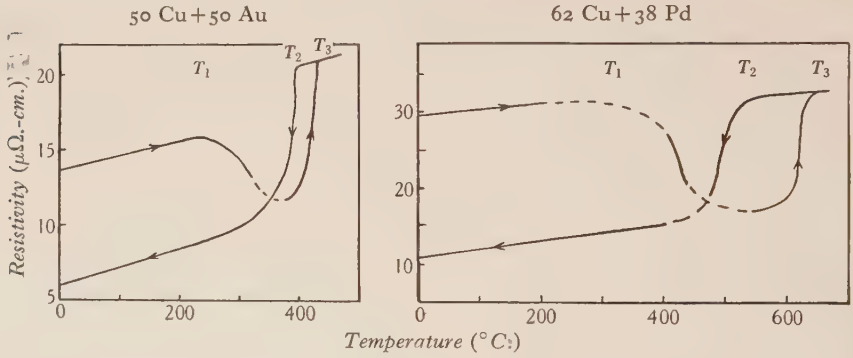

Figure 11. Hysteresis loops measured by Borelius, Johansson and Linde[37].

(not too near T_2) without showing any signs of beginning a transition into order. Thus we found a well-established hysteresis in CuAu and CuPd, whereas we estimated the transitions of Cu_3Pd to be without hysteresis. The recent very thorough examinations Cu_3Au by Sykes and Evans[50] have shown that there is also in the case of Cu_3Au a well-marked hysteresis though only extending over a few degrees on the temperature scale.

The transition between ordered and disordered states implies a mutual exchange of places of atoms two by two. It is clear that a slowness of this exchange will, by rapid cooling or heating, cause the state of the alloy to lag behind its stable state and thus gives rise to a hysteresis loop. This type of hysteresis has been mathe-

matically treated by Bragg and Williams[45]. It will be expected to be less pronounced the higher the temperature. As, however, the hysteresis found by our measurements was very pronounced also at temperatures at which we must expect a lively exchange of places of the atoms, we found it necessary to ascribe the hysteresis to thermodynamically metastable states and it was shown[44,45] that such metastable states were to be expected for certain types of the free energy F as a function of temperature T and degree of disorder ξ shown in figure 12. Point a represents a metastable state in heating, and point b in cooling, c represents stable states. Even where the free energy is not of this type a certain hysteresis could be expected thermodynamically as a result of internal stresses. There has been some doubt[45] whether such theoretical metastable states could really account for the hysteresis observed but, so far as I can see, no better explanation has as yet been given.

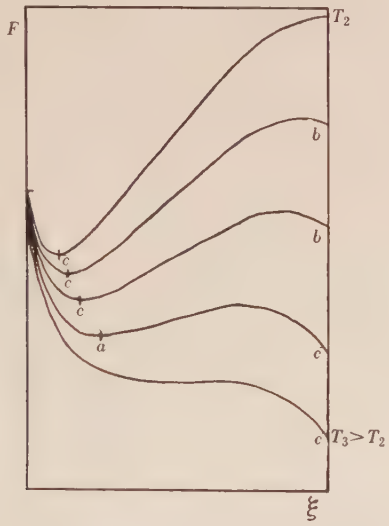

Figure 12. Isothermals of free energy F as a function of degree of disorder ξ according to Borelius[44].

§ 10. HYSTERESIS AT THE SEGREGATION PROCESS

The idea of relative minima of free energy as a cause of hysteresis of the superlattice transitions led to a search for similar phenomena in connexion with the segregation of a homogeneous alloy into two phases, and in fact resistance measurements of the system AuPt have given a very good support for this idea. As was found by Johansson and Linde[3], AuPt alloys of all concentrations can be brought into a homogeneous solid state by heating to sufficiently high temperatures. If these homogeneous alloys are quenched to say 800° C., where there is in the stable state a gap in the solubility from 25 to 90 atomic per cent Pt, the free energy of the homogeneous alloys obtained by quenching will, as was calculated by the author[53] from the equilibrium diagram, depend on the concentration approximately in a way shown in the upper section of figure 13. From a to d the homogeneous alloys are unstable. From a to b and from c to d where the curve is bent upwards the segrega-

tion that has to begin as a small increase of the Pt concentration in certain regions and a small decrease in the neighbouring ones will first cause an increase in the free energy and thus to a certain extent be prevented. The resistance measurements of Johansson and Hagsten[54] on an alloy with 30 atomic per cent Pt, and unpublished measurements of Wictorin on alloys from 25 to 50 per cent Pt agree very well with these expectations. The lower section of figure 13 shows the decrease in resistance,

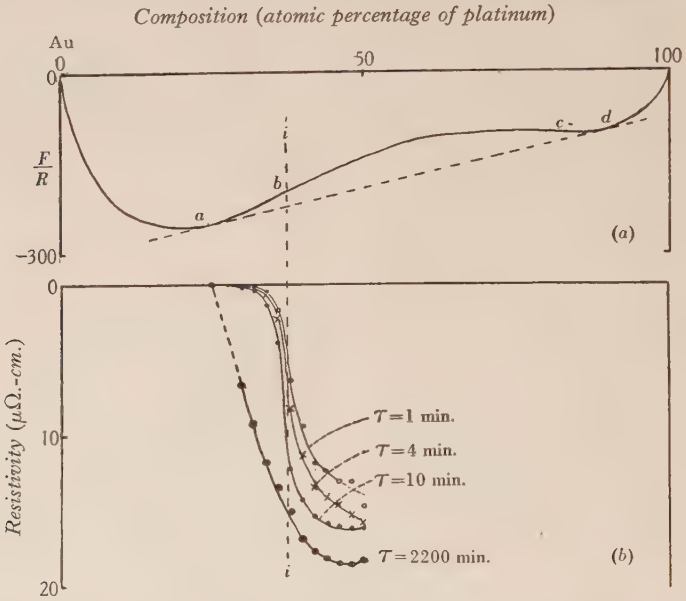

Figure 13. (*a*) Free energy of AuPt alloys at 800° C., calculated from the equilibrium diagram. (*b*) Decrease in resistance by segregation at 800°. (Unpublished measurements by Wictorin.)

here a measure of the segregation, for alloys first quenched in the homogeneous state from high temperatures to 800° C., then held there for τ min. and finally quenched to room temperature. The curves for small values of τ show points of inflexion at a concentration *ii* corresponding to the calculated inflexion in the free-energy diagram. Similar results are obtained at 900° and 700° C. When the free-energy curve is strongly bent upwards, in spite of the high temperatures and the probable high mobility of the atoms, the segregation is still a very slow one. The reverse process, the reconstitution of an homogeneous alloy, presents no such obstacles.

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A STUDY OF THE ORDER-DISORDER TRANSFORMATION

By W. L. BRAGG, C. SYKES and A. J. BRADLEY

§ 1. INTRODUCTION

The present account is a summary of a series of related researches into the order-disorder transformation, carried out at Manchester University and in the research laboratory of Messrs Metropolitan Vickers. Our researches have been planned to take their places in a concerted scheme, and it is hoped that this general summary and the list of papers at the end of this article will be a useful indication of their scope. Similar researches have been in progress in other laboratories. Though this account is restricted to the researches at Manchester, it is published with full acknowledgement of the work carried out elsewhere, particularly by Borelius, Dehlinger, Johannson and Linde, and others.

The order-disorder transformation has been followed by means of X-rays by Bradley and his coworkers. The theory of the transformation has been developed by Bragg and Williams, by Bethe, and by Peierls. The measurements of the changes in internal energy, in conductivity, and in some cases in magnetic properties, have been made by Sykes. A résumé of the programme of work in hand is given at the end of the article.

§ 2. THE GENERAL NATURE OF THE ORDER-DISORDER TRANSFORMATION

Examples of the order-disorder transformation and of its effect upon the physical properties of alloys are to be found in Bradley and Jay[1,2], Bradley and Rodgers[3] and Sykes and Evans[4]. All transformations as yet observed in binary alloys occur when the proportions of the constituents are approximately in the ratio 1 : 1 or 1 : 3. In the disordered state observed at high temperatures the atoms A and B of the two metals are arranged at random amongst the position of a pattern such as the face-centred at body-centred cubic lattice. In the ordered state at low temperatures atoms of each kind segregate into regular positions. For instance, in the classic case of Cu_3Au gold and copper atoms are distributed at random amongst positions of a face-centred cubic lattice when the temperature is high, whereas gold atoms occupy cube corners and copper atoms face centres in a regular way at low temperatures. There are other more complex cases when more than two types of atoms are involved, such as the Heusler alloy Cu_2MnAl or the alloy Fe_2NiAl. In the latter, corners of cubes are occupied by Fe and Ni in a random way, centres by Fe and Al in a random way. The ordering process is thus restricted to a distinction

between Ni and Al, but does not extend to a distinction between either of these and iron. We may compare the ordering phenomenon to the passage of the alloy through two successive processes of crystallization on cooling. In the first process the liquid becomes a crystalline solid. Atoms take up positions at regular sites, for instance those of a face-centred lattice, but there is as yet no distinction between atoms of either kind A and B. As the temperature falls still farther, a second crystallization within the solid crystalline lattice takes place, by the segregation of the atoms into regular positions. In both cases there is an increase of regularity, implying a decrease in the entropy and a decrease in the internal energy. This alteration of internal energy is the latent heat of fusion in the first case, and something analogous to a latent heat in the second case. There is an important difference between the two cases. At the freezing-point the substance passes over completely from the random arrangement of the liquid to the ordered arrangement of the solid. Intermediate states between liquid and solid would have an extremely high internal energy, and therefore the substance does not pass through them. Bernal has illustrated this feature by a striking two-dimensional model[19]. If a number of non-overlapping circles are drawn on a sheet of paper, they must either be packed in an orderly way, or there must be numerous gross misfits of contact; a series of slight misfits is geometrically impossible, unless we permit circles to overlap which implies large internal energy of strain. On the other hand, intermediate stages between complete order and disorder involve no excessive values of the internal energy. When crystallization of the second kind sets in, it is at first one of partial order and theoretically does not become one of complete order until the absolute zero is reached. Actually it is nearly complete at 100 or 200° C. below the temperature at which it starts. The ordering goes on over this whole range, and latent energy is evolved in cooling or absorbed on heating. Thus what corresponds to the latent heat of the first crystallization is spread out into an abnormally high specific heat over a wide temperature range in the second crystallization.

Although the completion of ordering is so gradual, it sets in at a sharply marked *critical temperature*. We can see that this must be the case by considering the reverse process of heating the ordered alloy. At first the passage of each atom from an ordered to a disordered position involves a certain amount of work V_0 required to thrust it out of relation to its ordered neighbours. As temperature increases there is an increase in the energy kT which determines the number of atoms in the state of higher energy, and at the same time there is a decrease in the energy V required to move an atom to a position of disorder, because each atom has more neighbours already disordered. These two variations so interact that there is finally a catastrophe, or complete breakdown of general order, at the critical temperature. The critical temperature corresponds to the Curie point of a ferromagnetic. In the general case, there is first a jump from a state of disorder to one of partial order with latent heat at the critical temperature and then a gradual increase of order as temperature falls. In special cases the alloy may pass continuously through all intermediate stages of order; the critical temperature is marked by a peak in the specific heat, but no latent heat is involved or absorbed.

So far it has been assumed that the alloys are in thermodynamical equilibrium at each temperature. Actually at temperatures below 200 or 300° C. the atoms interchange position very sluggishly. The influence of the rate of relaxation upon the degree of order must be studied. It is possible to freeze some alloys in the disordered state by quenching (we may compare them to supercooled liquids). It will be seen below, however, that the slowness with which they devitrify back into an ordered scheme is not so much due to sluggishness of atomic interchange as to the establishment in them of numerous nuclei of order which are out of phase with each other.

§ 3. THE THEORY OF THE DEPENDENCE OF ORDER UPON TEMPERATURE

The order-disorder change provides a very interesting exercise for thermodynamic theory. It may be considered in two ways. At a given temperature there is a partition of the atoms between ordered and disordered positions depending upon the amount of energy V required to move an atom from the ordered to the disordered position. A further assumption as to the dependence of this energy upon the existing degree of order establishes an equation for equilibrium at that temperature, and so leads to the general relation between temperature and degree of order. Alternatively an expression for the free energy F of the alloy in any given state of order may be formed. Since $F = U - TS$, an assumption as to the dependence of the internal energy U upon the degree of order must be made, based on the mutual potential energy of like and unlike neighbours A and B. The entropy S can be calculated from the number of complexions of the given state of order. The condition for equilibrium is then expressed as $\partial S/\partial\sigma = 0$, where σ is a parameter defining the degree of order. The two methods are of course equivalent and lead to the same equation. The latter method has been used by Borelius and by Dehlinger, the former by Bragg and Williams. The particular interest of the order-disorder change is that the entropy S can be calculated by first principles, since it simply depends upon the number of permutations of the atoms A and B. In this respect it is so much simpler than the change between liquid and solid, or between one allotropic modification and another.

Bragg and Williams[5] calculate the degree of order as a function of temperature, for cases where the atoms are in numerical ratios 1 : 1 and 1 : 3. The energy V is supposed to be proportional to the average degree of order of the whole surrounding structure.

Bethe[10] carries out the far more complex calculation of the dependence of order on temperature on the assumption that the mutual potential energy depends upon nearest neighbours alone. When this assumption is made the new and highly interesting feature of local order appears. If it be assumed that the ordering energy V depends on the general scheme of order of the whole structure, then V becomes zero with the vanishing of long-distance order at the critical temperature. If, on the other hand, V depends upon nearest neighbours only as Bethe assumes, we find that, although long-distance order vanishes at the critical temperature, nuclei of

local order persist. Schemes of order over restricted volumes are constantly appearing and being broken up, because it is always more likely that the nearest neighbour to an A atom will be a B atom rather than an A atom. Experiment as will be shown below indicates that Bethe's assumption is in closer accord with fact. Local order still has the effect of reducing the entropy and increasing the specific heat even above the critical temperature.

Bragg and Williams[11, 12] contrast the predictions based on their earlier hypothesis and on that of Bethe with the results of Syke's experiment (see below), and the theoretical treatment is amplified. Peierls[13] extends Bethe's treatment to the case of superlattices such as Cu_3Au with a 3 : 1 ratio between the two types of atom. Bethe has confined himself to the case of the ratio 1 : 1. Cu_3Au has been experimentally investigated rather completely, and comparisons between theory and experiment can be made. Neither the assumptions of Bethe nor of Bragg and Williams give a close agreement with the observed energy-temperature curve, but there is sufficient correspondence to prove that theory is on the right lines.

§ 4. MEASUREMENTS OF ENERGY CHANGES DUE TO THE FORMATION OF THE SUPERLATTICE

The progressive disappearance of superlattice order as temperature is increased is marked by an abnormally high specific heat due to the energy required to transfer atoms into positions of disorder, and by latent heat at the critical temperature where the long-distance order is finally destroyed. In special cases, there is no latent heat because the alloy passes through all stages of order. Above the critical temperature the specific heat should still be slightly above the normal value* due to local order. The measurement of the specific heat for the purpose of testing the theory requires accurate determinations over temperature intervals of a few degrees. Apparatus involving a new principle has been evolved for this purpose by Sykes[7, 16] and has proved to be very successful. The temperature of an outer massive metallic container is raised at a regular rate by a heating coil. The specimen inside the container is also warmed electrically by a measured energy input, which is so controlled that the temperatures of the specimen and container remain closely the same. The apparatus is evacuated. Corrections can be made for the very small heat losses or gains. Difference of temperature between specimen and container can be measured by a thermo-element very exactly indeed since it is so small, and the rate of rise of temperature of the container is accurately known since it can be measured over long time intervals. Hence the data for highly accurate specific heat determinations over short temperature ranges are available.

The features prophesied by theory are all present. The alloys show abnormally high specific heats rising to a maximum just below the critical temperature. The alloy Cu_3Au displays latent heat at the critical temperature, but β brass (CuZn) has

* There is no direct way of measuring the "normal" specific heat above the critical temperatures, but it can be inferred from the specific heat at low temperatures or the behaviour of alloys of other compositions.

none. Above the critical temperature the specific heat is slightly higher than a normal value for pure metals.

§ 5. TIME OF RELAXATION

An alloy at a given temperature not initially in the state of order characteristic of that temperature will relax towards it at a rate dependent upon the frequency with which atoms interchange their positions. The equation for the time of relaxation τ should have the form

$$\tau = Ae^{W/kT},$$

where A is a constant (of the order 10^{-9} to 10^{-12}) and W measures the energy barrier which has to be surmounted for interchange to take place. The above assumes that we are dealing with a simple case of an alloy in which a general scheme of order is established, but where the number of atoms in ordered positions is not in correspondence with equilibrium. Experiment shows that the actual state of affairs is not so simple (Sykes[14]). It is possible to obtain Cu_3Au at room temperature in a state which is apparently one of disorder as judged by its electrical resistance, by quenching it from above the critical temperature. Measurements made on the relaxation of the alloy back to the equilibrium state cannot be explained by a simple law of the type $\tau = Ae^{W/kT}$. Further, it is known that copper and gold diffuse into each other quite rapidly at 200–250° C., whereas the critical temperature is 391° C. If diffusion takes place at 250° C., atomic interchange at 391° C. should be so extremely rapid that no quenching could be fast enough to preserve the disordered state. Sykes has explained the discrepancy as being due to the formation of antiphase nuclei. Ordering in Cu_3Au takes place by a segregation of the gold atoms at points of one of the four interpenetrating simple cubic lattices which build up its face-centred lattice. All four simple lattices are equivalent, and nuclei of order may start according to any one of four schemes. If numerous nuclei start and grow till they meet the interfaces of nuclei with different schemes (antiphase nuclei), there must be disordered regions, since the atoms at and near the interfaces cannot conform to both schemes. This appears to be the state of affairs in an alloy "frozen" in disorder. The conglomerate of antiphase regions is very stable. Sykes has proved their existence and measured their size by means of X rays. Their effect on internal energy and on electrical resistance has been measured[15]. The quenched alloy with its numerous antiphase nuclei has an electrical resistance at room temperature which fits upon an extrapolation of the resistance curve of the disordered alloy above the critical temperature. It behaves electrically, in other words, as if it were completely disordered. On the other hand, the internal energy is lower than would be expected for complete disorder, showing that some approach to ordering has taken place.

Sykes has further shown that if the alloy is soaked for 48 hours at a temperature only a degree or so below the critical temperature, the antiphase nuclei coalesce into large regions over which the scheme of order is consistent. Once the alloy has been brought into this state it remains in equilibrium as its temperature is raised or

lowered (even at fast rates), always provided the critical temperature is not exceeded. At low temperatures the alloy in this state has an electrical resistance like that of a pure metal tending towards zero as the absolute temperature is approached.

It is easy to quench Cu_3Au with its four schemes of order into a state resembling one of complete disorder. On the other hand, it is impossible to quench CuZn in the disordered state. This is probably due to the fact that the latter alloy has only two alternative schemes of order (cube corners or centres for Cu or Zn). Four types of antiphase nuclei can form a stable froth (the boundaries behave as if they had surface tension), but two types cannot do so. Hence CuZn always breaks down into large regions which have a consistent ordered scheme.

§ 6. THE INFLUENCE OF ORDER ON MAGNETIC PROPERTIES

The alloy Fe_3Al shows peculiar magnetic effects, having two Curie points. Sykes has shown[8] that this phenomenon is due to the ordering process. As the alloy in the disordered state cools from a high temperature it reaches a Curie point and becomes ferromagnetic. At a slightly lower temperature order sets in. This critical temperature is below the Curie point for the disordered state but above that for the ordered state, hence the alloy loses its ferromagnetism. On cooling further it reaches the Curie point for the ordered state and becomes ferromagnetic again. Very interesting effects are produced by varying rates of cooling and heating.

Bradley has studied the effect of order on the ferromagnetism of the Heusler Alloys[3].

§ 7. WORK AT PRESENT IN PROGRESS OR ABOUT TO BE PUBLISHED

Measurements have been made of the energy of ordering in βCuZn alloys which depart from the equiatomic ratio. These measurements are in satisfactory accord with theory[17]. The existence of a superlattice in β brass, hitherto only inferred from its behaviour, has been definitely proved by Sykes and Jones[16]. Powder photographs have been taken with ZnK_α radiation. The proximity of this wave-length to the absorption edges of Cu and Zn introduces an enhanced difference of scattering power which causes the lines in the powder photograph for which $(h+k+l)$ is uneven to appear.

Several alloys which show ordering with a 1 : 1 atomic ratio of constituents are being studied thermally, electrically, and by X rays, in order to check theory with more experimental measurements (AgCd, AgZn, MgCd, etc.).

The alloy Cu_3Pd, which it was hoped would behave like Cu_3Au, appears to be tetragonal in the ordered state. The transformation in Cu_3Pd is so sluggish that it may be possible to prove the existence of Bethe's local order by direct methods, quenching and annealing from a temperature above the critical temperature.

The relation between size of antiphase nuclei as measured by X rays and their influence on electrical resistance is being studied.

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AGE-HARDENING ALLOYS

By C. H. DESCH, National Physical Laboratory

THE object of this short note is merely to call the attention of physicists to certain effects observed in alloys, of great technical importance, the explanation of which will have to be sought in the properties of the lattice, and in the changes of energy with temperature in lattices composed of more than one kind of atoms. The literature of the subject is very extensive, and has been reviewed by a number of recent writers.

The effect known as age-hardening, in which an alloy, after being heated and quenched, increases in hardness either spontaneously or on heating to a temperature below that of quenching, depends on the properties of supersaturated solid solutions. In order that an alloy may show this effect, it is essential that a solid solution be formed at a high temperature, from which a second phase can separate on cooling slowly. Quenching retains the solid solution in a supersaturated condition, and reheating causes precipitation, usually in a finely divided form. A marked change in solubility with temperature is essential, but the actual amounts vary widely in different alloy systems. Thus in the iron-nitrogen system the saturated solid solution contains only 0·05 per cent N at 700° C., whilst in the iron-molybdenum alloys the imit is 35 per cent at 1440°. Usually the quantity of the precipitated phase is only a small fraction of the solvent metal, but in the alloy of atomic composition Fe_2NiAl, studied by Bradley, the two phases which separate are in equal quantity.

Prolonged heating at a temperature below that of quenching leads to softening, and when the heating has been continued until particles of the second phase have reached such a size as to be easily visible under the microscope, the maximum hardness has always been passed. The original explanation of age-hardening by Merica, Waltenberg and Scott[9] was based on these facts. It was supposed that precipitation began in the form of very minute particles, and that these agglomerated with continued heating, a certain critical dispersion, below the limits of visibility in the microscope but not otherwise defined, producing the greatest hardness. In broad outline, this view still holds good, at least for those alloys which are hardened by heating, although minor modifications have become necessary. The chief difficulties in its application have arisen in dealing with alloys which harden at atmospheric temperatures, including those light alloys of aluminium in which the effect was first discovered. The nature of the later stages, in which agglomeration and softening take place, is not disputed, but there are differences of opinion regarding the processes which occur before the appearance of detectable particles.

In most age-hardening systems, the phase which can separate on slow cooling is a compound of the two metals, or at least an intermediate phase composed of two

kinds of atoms. There is, however, one important exception among alloys which have been studied in detail. This is the system copper-silver, in which hardening occurs by the separation of the pure metals. Copper and silver have identical space lattices, although their atomic diameters differ by 13 per cent, yet appreciable hardening can occur on suitable treatment. Any explanation of age-hardening must account for this simple case as well as for those in which precipitation of a new intermediate phase can occur. The hardening effect is considerable, an alloy with 6·6 per cent of copper, for instance, increasing from 50 to 140 Brinell at 250°[12].

The first objection to the simple hypothesis of hardening by critical dispersion came from determinations of the electrical resistance during the process. The quenched alloy, being a supersaturated solid solution, usually has a higher resistance than the same alloy in the annealed state, when separation into two phases is complete. Any partial separation, as required by the hypothesis of dispersion, might then be expected to cause a fall in resistance. This actually occurs with many alloys, but duralumin was found by Fraenkel[2,3] to show an initial increase when aged at atmospheric temperature, decreasing normally later. This fact, confirmed for some other alloys, including those of aluminium with small quantities of copper, caused Konno, Fraenkel, Sachs and others to maintain that hardening was caused by the movement of dissolved atoms to new positions in the lattice, favourable to the production of molecules, but causing local strains, thus increasing both hardness and electrical resistance. Rosenhain[10] suggested that, taking the original view, the first production of ultra-microscopic particles would produce such local strains in the lattice as to account for the increase in resistance, thus to some extent reconciling the two views, as the critical dispersion might even be on a molecular scale.

The increase of resistance in the early stages of hardening is not confined to those alloys which "age" at atmospheric temperatures. It is well marked in the alloys of copper with beryllium[8], in austenite containing titanium[13] and in several systems, mentioned below, which are not usually classed as age-hardening, but in which an increase of hardness accompanies precipitation.

The maximum resistivity, when it occurs, is reached before the maximum hardness, and, as shown by Masing, Köster, and others, when various properties which change during ageing are plotted against the time, the maxima do not coincide. It has also been shown by Gayler[5] and by Cohen[14] that two maxima may sometimes be found in the hardness-time curve.

Gayler and Preston[4] regarded the process as taking place in two stages: (1) the rejection of atoms of the dissolved metal from the lattice of the solid solution, with the formation of chemical molecules in certain instances, and (2) the coagulation of these atoms or molecules to form discrete particles. A more elaborate view of the process has since been given by Gayler[5]. Tammann[11] considered that the rejected atoms must collect on certain planes of the parent lattice, and that only when many neighbouring planes are so occupied can precipitation occur. This view has been confirmed by much later work by Mehl, Masing, Fink and others, which shows that the particles tend to group themselves to form minute plates

or needles parallel with certain crystalline planes or directions in the parent lattice.

The main process is clearly one of diffusion. In accordance with this, when the logarithm of the time taken to reach a maximum value of a property, such as hardness, is plotted against the reciprocal of the absolute temperature, a straight line is frequently obtained[7]. The initial stage of the process is, however, the reverse of diffusion (which always tends towards greater homogeneity) since it involves the segregation of certain atoms from a lattice on which they are distributed with statistical regularity. This process is not confined to age-hardening alloys, but must occur whenever one solid phase separates from another. The metallurgist, then, seeks an answer from the physicist to this question: what are the forces which lead to the expulsion of certain atoms from the lattice of a solid solution when the temperature falls to a certain point or when, the solid solution having been preserved in a supersaturated condition by quenching, the temperature is raised? (Alloys which harden at atmospheric temperature fall under this condition, as they are quenched at a lower temperature and do not harden if kept sufficiently cold, as, for instance, when quenched duralumin rivets are preserved in the soft state in solid carbon dioxide.)

The conditions are different from those of a solid crystallising from a liquid. The formation of nuclei of the solid phase by chance collisions is easily understood, but the movement of metallic atoms over a distance of many lattice spacings, making the structure less homogeneous, is more difficult to picture. It must occur very locally, since in the early stages no change in the lattice parameter can be detected by means of X rays.

In the discussion on Dr Gayler's paper[5], Prof. Mott remarked that groupings of, say, five atoms each would have a marked effect in increasing the electrical resistance of the lattice, so that the maximum resistance found in many, but by no means all, age-hardening alloys, must correspond with a very early stage in the formation of nuclei. Such nuclei once formed and the statistical uniformity of the lattice having been destroyed, local concentration gradients exist, and the rest of the process may be looked on as one of diffusion, the growth of the ultramicroscopic particles and their union to form larger masses being one which is very familiar in metallographic studies. The next question is, at what stage in the process will the greatest elastic strains be set up in the lattice, tending to increase the hardness and, to a lesser degree, the electrical resistance?

When the phase which is ultimately precipitated is composed of two kinds of atoms, as in hardening caused by $CuAl_2$, Mg_2Si, or Cu_3Be, what the chemist has been accustomed to call chemical affinity may be supposed to encourage the formation of groups approaching simple atomic ratios, but the separation of nuclei of copper from silver, or of silver from copper, cannot be accounted for in this way, yet the mechanism seems to be the same in each case. (That in the silver-copper alloys no increase in electrical resistance occurs during ageing, is probably due to the close similarity of the silver and copper atoms.) Both in the simple and in the complex examples, the separation occurs along the most closely packed planes in

the lattice, and, in those alloys which have been examined in detail, in such a way that the new phase, when formed, is produced with a minimum rearrangement on those planes, so producing *Widmanstätten* structures on a small scale.

There is reason to believe that nuclei of appreciable size exist long before a change in the parameter can be detected by X rays. It must be emphasised that the segregations are very local, leaving the greater part of the lattice unchanged. Such changes in the quantity of background scattering as have been recorded are consistent with such a picture of the process. It is remarkable that chemical methods seem to be capable of detecting an earlier stage. It was first noticed that in the hardening of the beryllium-copper alloys the etching properties were altered at a very early stage, so that, although no separate particles could be seen under the microscope, lines parallel with (111) planes darkened on etching, producing a fine network, indicating a precipitation of ultra-microscopic particles. The same thing is seen in silver-copper alloys, and it is probably responsible for the characteristic etching properties of martensite in steels. That it could not be seen in the light alloys of aluminium was used as an argument for the special character of the hardening process in them, but the writer has always attributed its absence to the lack of delicacy of the methods in use for etching aluminium. Fink and Smith[11] found that in a light alloy containing 5 per cent of copper, precipitation could be seen after heating for an hour at 100°, whilst 34 hours at that temperature were required to produce a measurable change in the lattice parameter. Even at atmospheric temperature precipitation could be seen after three months, which is of course much longer than is needed to produce hardening, but indicates that the process is of the same kind as at higher temperatures. Aluminium containing magnesium gave similar results.

This hurried survey of the age-hardening problem leaves out many complications—the effects of heating to a higher temperature after partly ageing at a lower and so on—but it is suggested that the mechanism of age-hardening may not be very complex. The original theory was probably too simple, in that it considered only changes in the sizes of the dispersed particles, and did not take account of how those particles came into existence, but in the writer's view it remains essentially true although the critical dispersion must now imply a stage earlier than that at which it is proper to speak of a distinct phase. The work on order-disorder changes has made us familiar with systems in which local rearrangements can occur without producing a second phase in the ordinary sense.

The complex changes in age-hardening may then be due only to the progressive growth of nuclei formed by the rejection of certain atoms from the lattice. The electrical resistance seems to be most affected by the formation of groups of only a few atoms, the hardness by groupings of a rather larger size, and so on. (The subsequent fall of resistance and later of hardness as the groups grow larger presents no difficulty.) Effects on the magnetic properties are not produced until still later[15, 16]. It is the initiation of the process, as mentioned above, that is difficult to picture, on which the advice of physicists is sought. The next problem is that of applying to age-hardening systems the same quantitative treatment that

has proved successful in dealing with order-disorder transformations (Bragg and Williams, Borelius, Peierls, Sykes, etc.), so that it may be possible to predict the behaviour of a given system under given conditions of supersaturation.

A new phase separating from a solid solution does not always assume a dispersed form. The α phase in brass, for instance, separates on cooling the supersaturated β solid solution in large crystals. Nevertheless, it must pass through the preliminary stage of forming minute nuclei, and in its behaviour it then closely resembles an age-hardening system[(6)] although its supersaturated solid solution has a lower, and not a higher, electrical resistance than the two-phase system which is ultimately formed. It would seem that in these alloys the growth of nuclei to form distinct crystals is very rapid. Differences in what may be called the crystal habit of the precipitated particles account for many differences between alloys, and the reasons for such differences must be sought in the mechanism of the separation of the original particles and their subsequent growth.

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DISCUSSION OF THE PAPERS BY BORELIUS, BRAGG, DESCH

Reported by N. F. MOTT

In the discussion Prof. Bragg emphasized the contrast between the order-disorder change, which extends over a finite range of temperatures, and the change from liquid to solid, which is sharp. He drew the attention of the conference to some speculations by Bernal* which attempt to show that intermediate states between liquid disorder and crystalline order would have very high energy and therefore do not occur.

Prof. Simon did not agree with Bernal's conclusion that no intermediate phase between solid and liquid can exist.

Both Prof. Fowler and Prof. Bragg were critical of Prof. Borelius' use of the free energy diagram in his discussion of hysteresis in the segregation process (Borelius, § 10). A rough calculation by Prof. Bragg of the life-time of the metastable states envisaged by Borelius suggested that it should be considerably less than 1 sec.

An extension of Bethe's theory of the order-disorder transition by Fowler and Chang to include interaction between next nearest neighbours was announced (to be published). Dr Sykes reported some new measurements of the heat content of CuZn up to the critical temperature, which agreed better with the new calculations than with the old; the new theory contains however an arbitrary parameter. A theory by Mott† of the nature of the ordering force also gives some indication of the shape of the specific heat-temperature curve.

Dr Sykes also reported measurements of the heat content of MgCd, which shows a latent heat at the critical temperature, in disagreement with the theoretical expectations, and also for Cu_3Pd, which does *not* show the latent heat to be expected for an alloy where the two constituents are present in unequal amounts. This may be connected with the change of structure which takes place for this alloy at the critical temperature.

In connexion with Prof. Borelius' measurements of the resistance of nickel, Dr Potter mentioned some recent measurements of his own (to be published shortly in *Proc. phys. Soc.*)

Dr Bradley gave an account of his investigations on the ternary alloys of the system FeNiAl. For certain compositions, alloys of this system would, if cooled slowly, crystallize out as a two-phase system, *both* phases having the same body-centred cubic lattice structure but with very slightly different lattice spacing, so

* *Trans. Faraday Soc.* **33**, 27 (1937).
† *Proc. phys. Soc.* **49**, 258 (1937).

small that it is very difficult to detect by X-ray methods. One of the two phases is magnetic, the other is non-magnetic and shows a superstructure.

If the alloy is cooled quickly (quenched) a single phase only is obtained. But if the alloy is cooled at a moderate rate, regions of undetermined size (say a hundred to a thousand atoms in length) form in the crystal, having the composition of one or other of the two phases that will eventually crystallize out, but arranged in a *single* body-centred lattice; they have not yet broken away and formed separate crystals with their individual lattice parameters. These regions must thus be highly strained; for their lattice parameters must necessarily be those of the parent lattice (i.e. the quenched alloy), whereas they would be in equilibrium only with different values of the parameters. Dr Bradley ascribed the properties which these alloys have as permanent magnets to this state of strain.

Prof. Bragg stated that the dispersion responsible for age hardening mentioned by Dr Desch must be understood in this way: groups of atoms having the compositions of the phases that eventually crystallize out would form, while still keeping to the old lattice. This would set up strains, and so produce hardening. The second process would be when these groups broke away from the parent lattice; this would decrease the internal strain, and thus the hardness.

Dr Peierls asked why the phase which is precipitated forms crystals with a plate-shaped structure parallel to a definite set of crystallographic planes. Two explanations seemed possible. The crystals might tend to form at internal surfaces of misfit, or cracks; this was favoured by Dr Desch. Prof. Bragg, on the other hand, considered that a given volume of a new phase could crystallize out with less strain to the surrounding medium if it took a plate-like structure than if it were, for example, round. He cited the case of felspar, which, if cooled, breaks up into bands containing alternately an excess of Na and of K. In this way the least strain is produced.

PART III

CONDUCTION IN THIN METALLIC FILMS

THE STRUCTURE OF THIN METALLIC FILMS

By G. I. FINCH

THE object of this paper is to draw attention to those structural features which are likely to give rise, at least in part, to the abnormally low conductance associated with thin metallic films[1]. The more usual methods for preparing such films in reasonably uniform thickness are (i) cathodic sputtering, (ii) condensation from the vapour *in vacuo*, (iii) chemical deposition and (iv) evaporation of a colloidal solution. Beaten leaf is generally too thick and irregular to be of use in conductivity measurements, and although electrodeposits can usually be freed from the basis metal their further transfer without injury to a non-conducting substrate is difficult.

Electron diffraction has become the most searching method for the study of the structure of thin metallic films. In addition to revealing crystal structure and orientation, electron diffraction will generally afford some indication of other features which are often of too fine a detail to be seen under the microscope, such as crystal size and shape and the nature of the film surface texture.

Consider, for example, the pattern (figure 1) obtained with the electron beam at grazing incidence from a bismuth film electrodeposited on to a polished copper surface. We see that (i) the film is polycrystalline; (ii) the crystals are unorientated; (iii) the pattern dimensions agree with the known structure of bismuth; (iv) the absence of ring-broadening due to refraction towards the central spot shows that the diffraction rings are formed by transmission; thus the diffracting portions of the crystals must project above the surface; (v) the ring definition suggests a size of effectively diffracting crystal projections exceeding 100 A. in directions normal to the beam but, in view of the clearness of the pattern and absence of general background, not exceeding about 200 A. in the beam direction; (vi) the granulated appearance of the rings shows that a relatively small number of crystal projections are diffracting, which suggests that the crystals are large enough to be seen in the microscope. Thus we can picture the general structure of the bismuth film as consisting of disordered array of fairly large crystals terminating in spikes projecting above the mean level of the surface, an impression which would be confirmed if a sharp and strongly granulated ring pattern were obtained by transmission through the film after its being detached from the substrate. It will readily be seen that if the average thickness of the film were only 10 A., the actual crystals could not cover more than one-tenth of the surface, and the film would be discontinuous apart from small areas of contact between neighbouring crystals. Electron diffraction shows that the structure of very thin metallic films with an average thickness of the order of 50 A. and less is in general of this type.

Again, from figure 2, yielded by a platinum fibre sputtered in argon on to a polished glass disk, we see that the platinum crystals are strongly orientated with a cube face parallel to the substrate. The increase in width of the arcs which occurs as the pattern centre is approached is evidence of a refractive effect and shows that the pattern has been formed partly by reflection, i.e. entry and exit of the beam through the same flat crystal faces, in this case (001) faces; since the individual diffractions are not wholly displaced but are spread out between the normal and refracted positions, it is clear that diffraction through projecting crystalline spikes of a wide range of acuteness also occurs. The same film by transmission with the beam normal to the surface gives a complete ring pattern in which the *hko* diffractions are abnormally strong. The rings show no signs of granulation and their width is such as to suggest a mean crystal size of the order of 50 A.

Figure 1.

Figure 2.

Caution is necessary in the estimation of crystal size from ring-breadth, especially in the case of reflection patterns. Thus, suppose a metal film of uniform thickness be deposited on a plane surface, the diffraction rings will be very broad, even though the crystals may be large, provided the deposit crystals form such obtuse-angled projections that only a small extent of each projection is thin enough to contribute to the diffraction of the beam. In such a case, if the film is sufficiently thin, a transmission pattern will give a better idea of the crystal size, and will confirm whether the diffuseness of the rings of the reflection pattern is due to the obtuseness of the crystal projections or to small crystals. On the other hand, a reflection pattern is likely to give a better impression of the particle size if the substrate surface be spiky and is more or less uniformly covered by the deposit.

Several workers[2] have ascribed the anomalous conductivity of thin films, prepared as a rule by cathodic sputtering or evaporation, to their supposed amorphous nature. Electron diffraction results negative this view; thus it has been found generally that cathodically sputtered and evaporated metallic films are invariably crystalline, even when deposited at liquid-air temperatures[3]. There is, however, a

pronounced tendency for the crystal size to increase with the temperature of the substrate during deposition. Sputtered films often contain occluded gas, or the metal may even combine with gas in the process of deposition, though by sputtering in carefully purified argon this effect can be reduced[4]. The presence of gas in sputtered films no doubt explains the disappearance of the reflection diffraction pattern from sputtered platinum films during heating *in vacuo*, a result which was first attributed by Finch and Ikin to a reduction in crystal size. More recent experiments in which such heated platinum films were floated off the glass or quartz substrate by a weak solution of hydrofluoric acid revealed, however, a well-developed crystal structure, in that the films yielded sharp ring patterns on transmission. Hence it seems clear that the fading of the initial reflection pattern with heating must have been due to a collapse of the projecting diffracting crystal spikes as a result of the evolution of gas occluded during sputtering, a view which is confirmed by the fact that we have found that platinum films formed by evaporation *in vacuo* give reflection patterns which are virtually unaffected by heating. In view of the uncertainties introduced by the presence of occluded, and often also by combined, gas, sputtered films can hardly be regarded as suitable for critical conductivity determinations.

The structure of films condensed *in vacuo* may be profoundly affected by the nature of the substrate. A pseudomorphic lattice change has only been observed in the case of metals of similar lattice constants and crystal structure in contact as substrate and deposit, and this complication from the point of view of conductivity measurements is therefore easily avoided. Crystalline substrates consisting of natural or cleavage faces of ionic single crystals are rarely, if ever, sufficiently smooth, and in addition they often exert very strong orientating effects. For example, most metals deposited on a suitably heated rock-salt cleavage surface are strongly orientated and may even form single crystal sheets with an orientation governed by the substrate[5]. In view of the difference between the metal and rock-salt lattice dimensions it is most unlikely that such sheets are true single crystals; more probably they consist of a mosaic of small crystals of like orientation. Further, in the case of rock-salt and similar cleavage surfaces, it is a moot point as to how far the substrate mosaic structure, cleavage striations and cracks may affect the continuity of the deposit film. On the other hand, extremely smooth non-conducting substrate surfaces, free in all probability from surface flaws and cracks, can be obtained by polishing; for example, the diffraction patterns obtained from polished diamond, quartz, sapphire and many other surfaces are such as to suggest that they are exceedingly smooth and crystalline, whilst polished fused quartz, glass, spinel and other surfaces give patterns which are characteristic of a liquid or vitreous surface[6].

While the orientation which occurs in a deposit formed on a single crystal surface may easily be complete in the sense that both directions of orientation of the deposit are controlled by the structure of the substrate, a twofold orientation has apparently never been observed on a vitreous surface, although an alignment of the deposit crystals with one plane parallel to the substrate surface is so often noticed as

to be the rule rather than the exception, particularly if the substrate was suitably heated during deposition.

It frequently happens that the useful life of a thin metallic film ends with the appearance of a fine network of cracks which in some cases may be due to a differential expansion as between deposit and substrate, and in others to contamination of the deposit by traces of organic materials[7]. Recent electron diffraction work has shown how easily contamination can occur with greases and mercury vapour[8]; hence in the preparation of thin metallic films for conductivity purposes the greatest possible care should be taken to eliminate such impurities. Lovell's[1] recent experiments have shown the great gain in reproducibility of results which follows when proper precautions are taken to eliminate such impurities and gas adsorption. Some workers have observed deviations from the normal lattice constants in thin films. Thus Riedmiller and Cosslett[9] found such an effect with indium and attributed it to gas occlusion: and Quarrell[10] has found similar deviations of lattice dimensions to be general in the initial layers of a deposit and, in the case of face-centred-cubic metals, attributed this to a gradual transition from a hexagonal close-packing of the atoms first deposited to the normal face-centred-cubic packing.

Ample evidence has been obtained for the rapid oxidation of evaporated metal films on exposure to air. Thus Finch and Quarrell[11] found such oxidation with zinc and magnesium, Beeching[12] with aluminium and copper, Riedmiller[9] with nickel, and Nelson[13] with iron. Thin metal films, especially when prepared by evaporation, are much more prone to oxidation than the surface of the metal in bulk. Beeching considers that oxygen may be taken up from the surface of the substrate, where it is present as an absorbed layer; this points to the importance of careful cleaning and degreasing of the substrates employed.

To sum up: For conductivity experiments it would seem advisable to use suitable highly-polished non-conducting substrates. Deposition should be carried out in a high vacuum, the necessary precautions being taken to prevent contamination by either grease, mercury or gas. Wide temperature fluctuations of the substrate should also be avoided both during preparation and use. It should not be difficult to determine the resistance of a film *in vacuo* and thus eliminate errors and uncertainties arising from gas adsorption or compound formation.

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SOME FACTORS INFLUENCING THE RESISTANCE OF THIN METAL FILMS

By E. T. S. APPLEYARD

§ 1. INTRODUCTION

A convenient summary of the early work on thin metallic films, performed prior to 1928, is provided by Bartlett[1]. The observations varied profoundly not only from one worker to another but also in the experiments of the same investigator performed under similar experimental conditions. As a result of these discrepancies, which arose partly from primitive technique and partly from uncontrolled factors whose importance was not then understood (condition and temperature of the substrate, adsorbed gas, etc.), various *ad hoc* hypotheses were produced to explain particular experiments and little advance was made towards obtaining experimental conditions which would give consistent and reproducible results. It would be useless to add to the already copious literature of speculation upon these early observations. This review is, therefore, confined to enunciating briefly and attempting to explain some of the chief experimental observations on the resistance of thin metal films prepared by evaporative deposition in a good vacuum. This method of preparation curtails considerably the number of arbitrary factors which can influence the resistance of the films; and in particular it gives some hope of minimising, if not eliminating, the effects due to adsorbed gas.*

§ 2. TYPICAL EXPERIMENTAL RESULTS

A usual and important type of experiment consists in allowing a calibrated beam of metal atoms to fall upon a cooled surface. Suitable electrical contacts allow the resistance of the film to be measured at frequent intervals as the deposition proceeds, and in this way the relationship between the nominal resistivity† and the nominal thickness† of the film can be obtained experimentally.

Typical of the results obtained by evaporation are those of Reinders and Hamburger[2]. These workers paid attention to the temperature of the depositing surface and they worked in a tolerable vacuum probably of the order of 10^{-6} mm. of mercury. (Nevertheless the apparatus could not be properly baked out since it contained greased joints.) The thickness of the deposits was obtained by chemical

* Nevertheless, even in the best available vacuum, say 3×10^{-8} mm. of mercury, 10^{13} atoms per second strike every square cm. of the internal surface of the apparatus if the residual gas is oxygen. This rate is quite comparable with the rate of condensation of metal atoms in most experiments.

† The nominal thickness of a film is the thickness calculated from the expression $t = m/\rho$ where m = mass of metal per unit area. It only coincides with the geometrical thickness when the film is uniform and has the same density as the bulk metal. The nominal resistivity is calculated by assuming that the nominal thickness is in fact the true thickness. Where we refer to "thickness" and "resistivity" without qualification they are assumed to be derived in this way.

estimation of the evaporated silver, thus avoiding recourse to speculative formulae which have been used in certain cases.

Figure 1, copied from the paper of Reinders and Hamburger, shows the results obtained for silver. Ordinates are logarithms of nominal resistivity in ohm-cm., abcissae are logarithms of the thickness in multiples of 10^{-7} cm. Curve a_3b_3 is the resistivity of silver deposited at room temperatures (300° K.), a_1b_1 deposition at 88° K., a_2b_2 the {resistivity, thickness} relation of films deposited at 88° K. and afterwards raised to room temperatures. For comparison the results of earlier workers are also sketched in; Vincent[3] (chemical deposition, 1901); Pogany[4] (sputtered films, 1916); Weber and Oesterhuis[5] (evaporation, 1916).

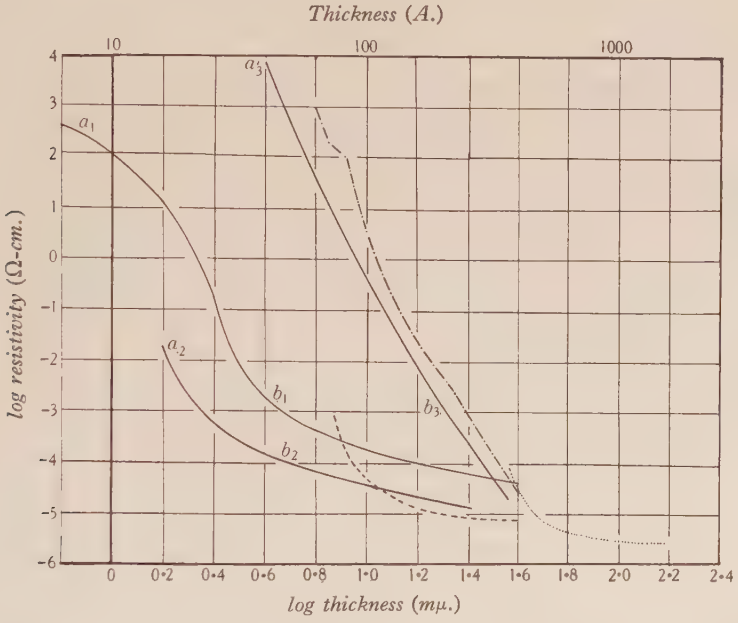

Figure 1. •—•—•—Weber-Oesterhuis; ———— Pogany; ••••••• Vincent.

It will be seen that Reinders and Hamburger were successful in obtaining detectable conductivity at only 6 A. thickness, or about two atomic layers. Nevertheless two important features stand out characteristic of all previous work on thin films.

The first is that the resistivity of films less than 100 A. in thickness is from 10^7 to 10^3 times that of the metal in bulk. The second is that the resistivity of the films alters irreversibly on heat treatment by a factor of about ten. Also deposition at 300 K. gives conductivity only at nominal thicknesses greater than 40 A. Reinders and Hamburger suppose that granulation of the film at the higher temperature accounts for this delayed conductivity, but they assume other causes to account for the high resistance of films deposited at 88° K. Before discussing the evidence for their interpretation we propose to describe in brief the results of certain experiments recently carried out in this laboratory on thin films of the alkali metals. These

results we believe to be interesting from two points of view: Firstly, because we believe that they are the only metal films ever prepared which can be obtained completely coherent in layers less than 50 A. thick; secondly, because by suitably varying the experimental conditions we have been able to prepare films of any resistivity desired from the extremely low value shown by the coherent films to values 10^5 times greater. We advance reasons for believing that these high resistivities are due to granulation or agglomeration of the film, and that agglomeration may account for both the delayed conductivity and the high resistivity of films prepared by many other workers, though further experiments are needed to decide definitely upon this point.

§ 3. LOW-RESISTANCE FILMS OF THE ALKALI METALS

The experimental methods of preparing these films are fully described in the papers of Lovell[6] and Appleyard and Lovell[7], so it will be sufficient to summarize the chief features of the apparatus and the experimental results.

The apparatus consisted of a molecular gun constructed of pyrex. The stream of atoms from the gun, suitably defined by cooled slits, struck a surface of pyrex glass which could be held at any temperature between 64° K. and 90° K. Here they formed a square patch overlapping end contacts of colloidal graphite spread upon a layer of platinum paint which had previously been burnt into the glass. Prior to any experiment the whole apparatus was baked out at 500° C. for several hours and carefully outgassed alkali metal was then distilled into the oven. The residual pressure varied between 5×10^{-7} mm. of mercury and 5×10^{-8} mm. of mercury and was usually near the lower limit. The results described below were not apparently at all sensitive to variations of this residual pressure.

A continuous series of resistance measurements carried out during and after the deposition showed always the same general character in the case of all the alkali metals. The resistance and the resistivity of the film fell steadily as the thickness of the layer increased. On stopping the deposition the resistance did not remain constant as was to be expected, but rose smoothly so as to increase by a factor of ten or more when the condensing surface was kept at 90° K.

But in the early experiments with rubidium, a consistent value could be obtained at first neither for the value of the resistance nor for the subsequent increase of resistance after deposition was stopped, and a series of experiments carried out under apparently the same conditions gave extravagantly different results, varying by factors of many hundred. The residual pressure and small variations of beam intensity proved to have no critical effect, and it was not until a casual observation forced upon our attention the important role of the surface conditions of the substrate that we were able to obtain consistent results. In Lovell's paper the technique of prolonged local baking necessary to produce a standard surface, upon which results consistent to 3 per cent could be obtained, is fully described.

The general character of the anomalies observed is best illustrated by showing the effect of deliberate contamination upon a surface previously baked to the standard state. Figure 2*a* reproduced from the *Proceedings of the Royal Society*[6]

shows the effect of CO_2 contamination upon a standard surface. The pressure in the apparatus was raised to 10^{-6} mm. of CO_2. The pressure was held at this value for some minutes, evolution of CO_2 was stopped, and as soon as the vacuum had reached its original value a distillation was commenced. Throughout the process the surface and defining slits were held at 90° K. The first distillation after this treatment gave no conductivity after 30 min. distillation of rubidium at the rate of $3{\cdot}18 \times 10^{12}$ atoms per cm.^{2} per sec.

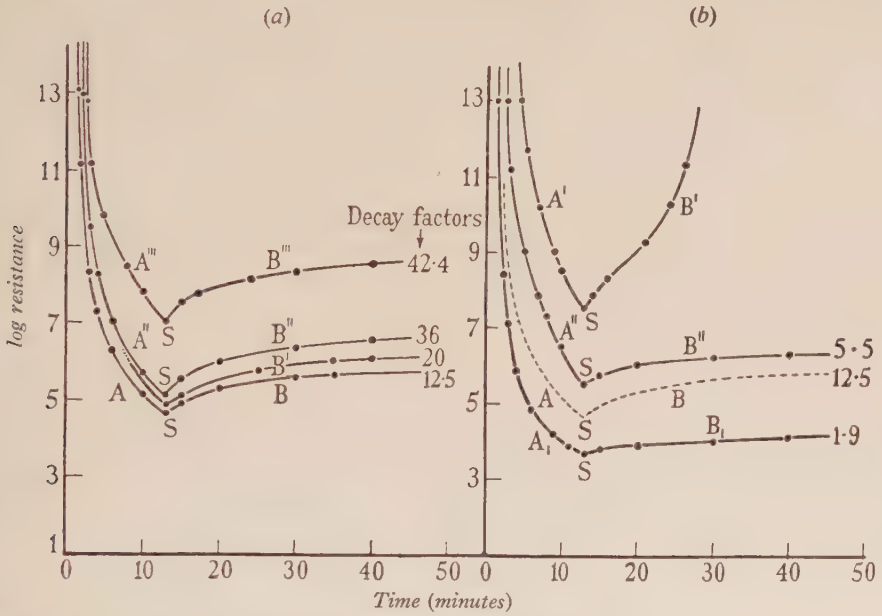

Figure 2.* Influence of contaminated substrate on the formation and decay of conductivity for films 21·8 A. thick deposited at 90° K. with beam intensity $3{\cdot}18 \times 10^{12}$ atoms/cm.^{2}-sec. (*a*) Influence of varying amounts of CO_2 impurity. (*b*) Influence of varying amounts of H_2O impurity. S, shutter closed (cessation of deposition); - - - - standard surface curve for comparison.

[*By the courtesy of the Royal Society*

Table I below shows the results obtained by successive baking of the substrate.

Table 1

Experimental curve	Total baking time before distillation (hours)	Remarks
A''' B'''	1	
A'' B''	20	
A' B'	40	
AB	80	Identical with results obtained on standard surface

The numbers to the right of the curves are the so-called decay factors, an arbitrary measure of the instability of the films. The factor is defined as $\Delta R/R$ where ΔR is the change in resistance during the half hour after stopping distillation, and R

* The decay factors are inserted at the right-hand side of all decay curves.

is the resistance when the deposition is stopped. The most important feature of the curves is their steady alteration as the heat treatment is continued, and the fact that they converge finally to the value characteristic of the standard surface after prolonged heat treatment of the surface.

Figure 2*b* represents the results of a series of experiments when water vapour and not CO_2 was the contaminating agent. $A'B'$, $A''B''$ represent successive curves obtained at different stages of the baking. The final steady state of the surface gave the curve A_1B_1 after prolonged baking, i.e. a lower resistance and a smaller decay factor than the standard surface which gave the dashed curve AB. Evidently the surface was permanently altered by its previous treatment and no subsequent baking ever restored it to the standard state. Probably rubidium hydrate was produced which gradually soaked into the glass.

These experiments forcibly draw attention to the manner in which the whole history and properties of an alkali metal film are determined by the surface condition of the substrate upon which the metal is distilled. We may now turn from these contaminated surfaces to discuss the results of investigations upon the clean standard surface prepared by prolonged baking.

§ 4. PRODUCTION OF STABLE AND COHERENT FILMS

A series of experiments carried out with rubidium deposited upon the standard pyrex surface cooled to various temperatures led to the following general conclusions

(1) For metal films of the same nominal thickness deposited at the same rate the decay factor diminished as the temperature was reduced, and parallel with this diminution of the decay factor the resistance also fell.

(2) The decay factor diminished as the nominal thickness of the film increased for deposition at a given temperature.

(3) By deposition at 64° K. (the lowest temperature available in the experiments) it was found possible to prepare completely stable films provided the nominal thickness exceeded 40 A. These films remained stable when afterwards raised to 90° K. though a film of this nominal thickness deposited at the higher temperature had the large decay factor of 3·5.

Figure 3 summarizes the results for rubidium.

Potassium and caesium give results of the same general character, except that potassium films were less stable and caesium films more stable than those of rubidium. The case of caesium is particularly interesting, for in this case by deposition at 64° K. stable films of nominal thickness only 5·7 A. were obtained. It was, however, not possible to determine the temperature coefficients of films as thin as this since they began to decay slowly when raised to 90° K. Another curious anomaly exhibited by the caesium films, in which they differ completely from those of potassium and rubidium, is that when deposited at any definite temperature the stability appears to be greater for films of 5·7 A. than it is for those of 24 A. After this thickness the films become more stable again as the thickness increases.

§ 5. RESISTIVITIES OF THE STABLE FILMS

The most obvious peculiarity of these films as compared with those prepared by all previous workers is their low resistivity at thicknesses below 100 A. For example, reference to figure 1 of this account shows that the silver films prepared by Reinders and Hamburger[2] had resistivities more than 1000 times those of the bulk metal at

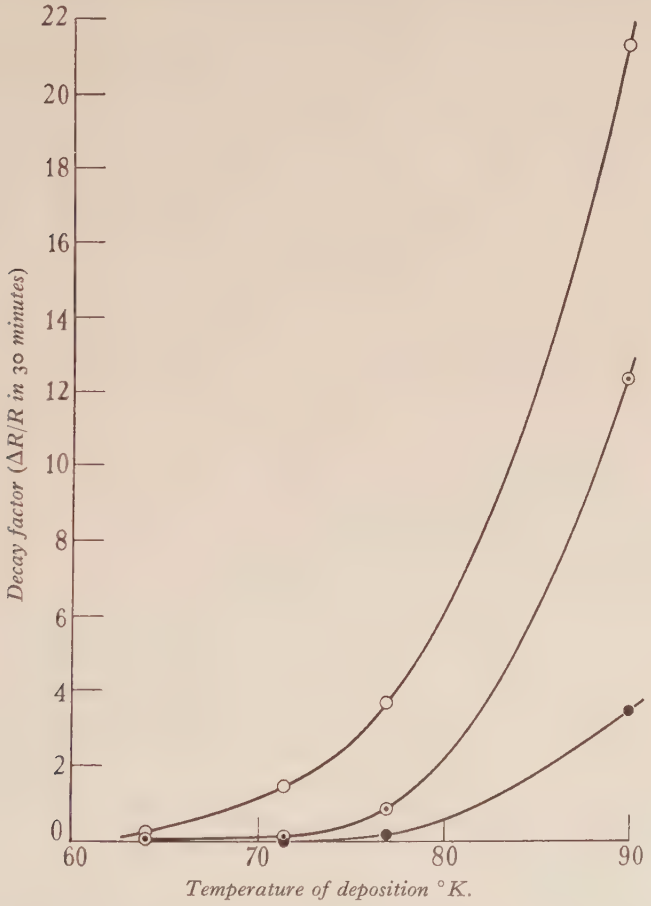

Figure 3. Decay factors as a function of the temperature of deposition for films of a given thickness deposited with beam intensity $3{\cdot}18 \times 10^{12}$ atoms/cm^2/sec. ○ 4·4 A.; ⊙ 21·8 A.; ● 43·6 A.

[*By the courtesy of the Royal Society*

a thickness of 40 A. Caesium films of this thickness deposited at 64° K. had only 5 times the resistivity of the bulk metal. Figure 4 below is a graph showing experimental resistivities plotted against nominal thickness for caesium deposited at 64° K. (full curve). Conductivity was first detectable at a nominal thickness of only 0·35 A. or 0·06 atomic layers. These facts lead us to believe that perhaps the films could be regarded to a first approximation as coherent slices of a crystalline, or polycrystalline, metal and that their resistivities (which were still higher than those

of the bulk metal) could be accounted for by assuming that the mean free path of the conduction electrons was effectively shortened by collision with the boundaries; an idea originally due to J. J. Thomson[8], who gave a formula for the resistivity to be expected.

Hamburger[9] had already applied Thomson's formula to much thicker films than this. His calculations contain so many qualifications that they cannot be said to show more than a sudden rise of resistivity when the thickness of the film became

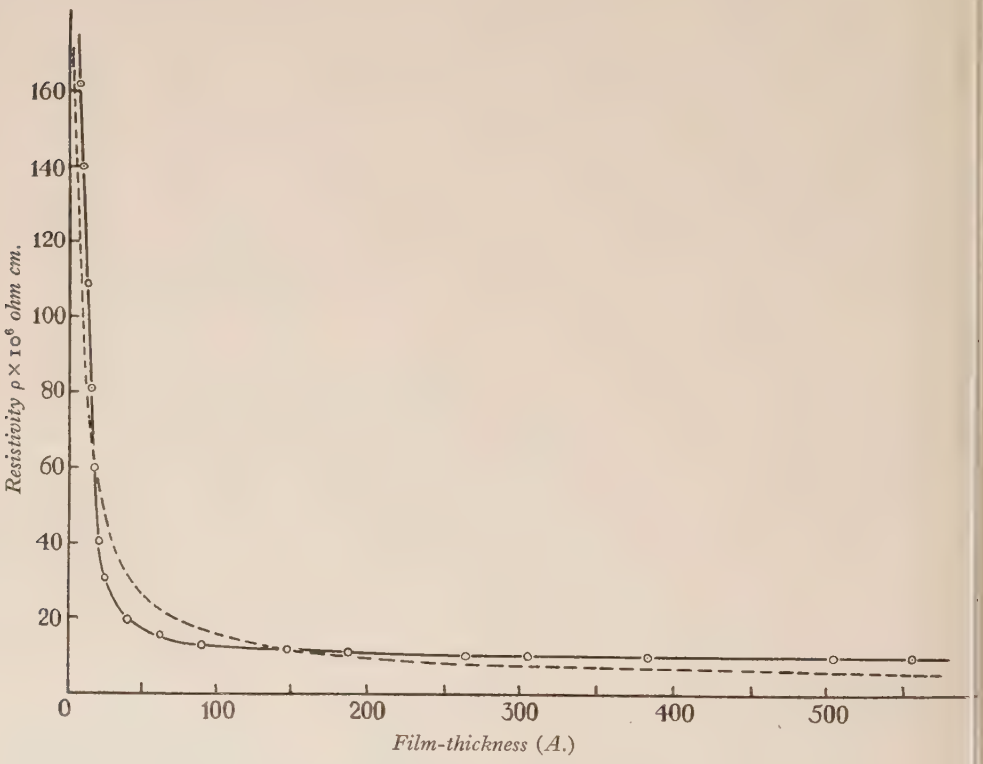

Figure 4. Theoretical - - -, and experimental ⊙. Resistivity/thickness curves up to 550 A. for a caesium film deposited at 64° K.

[*By the courtesy of the Royal Society*

comparable with the mean free path calculated on his assumptions. In any case, Thomson's formula was not applicable to our films, for in all cases the thickness here is very much less than the mean free path in the bulk metal, and Thomson took no account of the fact that, under these circumstances, most of the collisions will take place at the boundaries.

A modified formula[6] with which we have compared our results is

$$\frac{\sigma_t}{\sigma_\theta} = \frac{t}{\lambda_\theta}\left(1 + \log\frac{\lambda_\theta}{t}\right) \qquad \ldots\ldots(1),$$

where σ_t is the resistivity of the film and σ_θ that of the bulk metal at the same

temperature θ. λ_θ is the mean free path in the bulk metal, and may be deduced from the observed resistivity by the formula[10, 11, 12]

$$\frac{1}{\sigma} = \frac{Ne^2}{m}\frac{2\lambda_\theta}{v},$$

where N is the number of electrons (atoms) per unit volume and v the velocity of the electrons, given by

$$v = \frac{h}{2m}\left(\frac{3N}{\pi}\right)^{\frac{1}{3}}.$$

The formula is derived making two assumptions: firstly that $t \ll \lambda_\theta$, and secondly that all collisions of the electron with the sides of the film are inelastic. The values of λ_θ are, using accepted values for the resistivity of the bulk metal, 1980 A. at 90° K. in rubidium, 1450 A. at 64° in caesium. All the films described here are

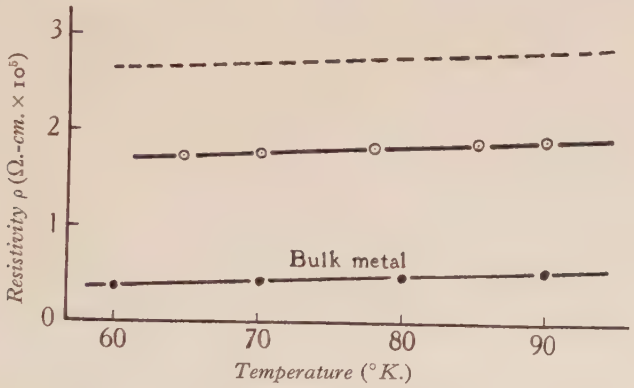

Figure 5. Theoretical - - -, and experimental ⊙. Resistivity/temperature graphs for a film 49·5 A. thick deposited at 64° K. ● bulk metal.

[*By the courtesy of the Royal Society*

less than 500 A. thick, though work with caesium films up to 12,000 A. is in progress (Lovell).

The broken curve in figure 4 is obtained by substitution in formula (1), and it will be seen that there is good agreement between the theoretical and the experimental curves. This is all the more satisfactory since formula (1) contains no adjustable constants, but yields at once absolute values of the resistivity. The worst disagreement occurs precisely where we might expect; where the film is so thin that it cannot be expected to show the properties of a regular lattice, that is, at less than 10 A., or two crystalline layers, and at large thicknesses where t becomes comparable with λ_θ.

Rubidium and potassium also show good agreement at thicknesses greater than 30 A., though here it must be remembered that the decay process previously mentioned tends to raise the resistance above the theoretical value since even at 64° K. the first layers put down are disintegrating appreciably.

The temperature dependence of resistivity of the stable films may also be calculated from formula (1), and figure 5 shows a comparison of the results for caesium

films 49·5 A. thick deposited at 64° K. It will be seen that they show a positive temperature coefficient.*

There seems little doubt that the explanation put forward above is correct in its broad features, but it is unlikely that the extremely simple assumptions put forward above are entirely correct. Calculations of a formula to replace equation (1) under more general conditions are at present being carried out by Fuchs.

§ 6. DISINTEGRATION OF THE FILMS. THE PHENOMENON OF DECAY

In references (6) and (7) a hypothesis is suggested which explains qualitatively all the phenomena of decay. The view put forward there was that the film was slowly tearing itself up under the influence of surface tension forces which in the thinner films may reach very high values; in a rubidium drop of radius 10 A. the pressure is of the order of 30 tons per square inch,† which is of the same order of magnitude as the ultimate tensile strength of carbon steel. Thus if a slice of an alkali metal could by some means be prepared about 10 A. thick it would immediately disintegrate if any cracks or imperfections existed at any point, because of the low elastic yield point of the alkali metals combined with the high stresses around any hole or crack. When the film is deposited upon a substrate the forces will however be profoundly modified by the magnitude of the surface energy at the metal-substrate interface and the film may become more stable.

Let us take a crude and concrete picture of the disintegrating film as a homogeneous metallic phase riddled with cracks and imperfections which are gradually widening under the influence of the surface forces. We regard these cracks as insulating barriers, the current being carried by bridges of unbroken film which become fewer and narrower as the disintegration proceeds. Assume that the continuous parts of the film are still thin compared with their linear dimensions measured along the surface. Then if E_1 is the surface energy of a free metal surface (necessarily positive) and E_2 is the (negative) surface energy at the metal-glass interface, it is clear that, fixing attention upon a definite geometrical configuration of the disintegrating film, the forces tending to disintegrate it further will be proportional to E_1+E_2. If E_1+E_2 is positive, as appears to be the case in these experiments, the film will continue to shrink away from the cracks, and to thicken up in the parts which remain intact until the curvatures at the free edges have enlarged so much

* The negative temperature coefficient observed in many early thin films is not explicable upon any simple theory of metallic conduction. It is indeed clear that no form of mere geometrical disintegration of the film (sponginess, porosity, etc.) can give a negative coefficient to a film if the bulk metal has the normal positive coefficient. The most that can happen is that the part of the resistivity due to strain in the lattice, and collision of the conduction electrons with the boundary, may swamp the temperature-dependent part to give a zero coefficient. Hence one may incline to the belief that perhaps septa of occluded gas between the crystals may account both for the negative temperature coefficient and the high specific resistance of such films. Even those prepared in vacuo classed as good by ordinary standards (tungsten[2], molybdenum[13]) cannot be guaranteed free from gas. Septa of gas have been suggested by Johnson and Starkey[14] to account for the high resistivity of certain mercury films.

† Drops as small as this contain relatively few atoms, so that the calculation is only correct as regards order of magnitude.

that the surface tension forces can no longer cause flow in the metal. It is conceivable that this flow also produces a violent cold working of the crystals which hardens them and also gives rise to a *Restwiderstand*.

The above simple view of the decay process accounts satisfactorily for most of the experimental facts in the case of the alkali metals investigated. It describes satisfactorily the diminished decay factor for films deposited at the lower temperatures. At the lower temperatures the mechanical rigidity of the metal is increased, and so the flow will not take place so quickly; also during the deposition when alkali metal atoms are being deposited on the bare glass the lower temperature will diminish the mobility of the atoms over the glass surface, and on this account too the formation of cracks will be hindered. It explains the fact that, all other things being equal, the decay factor diminishes as the thickness of the film increases in the case of rubidium and potassium. And what is perhaps most important it satisfactorily explains why a film which is stable when deposited at a low temperature remains stable when raised subsequently to a higher temperature. For, once a continuous film has been formed, surface tension forces can only act so as to diminish any surface irregularities which do exist. The effect upon the stability of the films of minute traces upon surface impurities on the substrate also is perfectly comprehensible, for it is well known that the surface forces of the type of E_2 are particularly sensitive to contamination of the surface. There is only one observation which is in serious disagreement with the suggested picture: the fact that in caesium there is a certain range of nominal thickness over which the decay *increases* with the thickness. This suggests that the conception of the metal as a homogeneous phase may need reconsideration, as is mentioned later.

Lovell's results (unpublished) for potassium, rubidium and caesium show that only in the case of caesium does the resistivity of thick films converge to the value given for the ordinary bulk metal. Both potassium and rubidium give values about double the bulk resistivity but unfortunately the results so far obtained for rubidium are not very reliable. In the case of potassium, however, the excess resistivity can be accounted for as a *Restwiderstand* due to strain. Some of this strain can be relieved by annealing at 90° K., and a similar, though much smaller strain seems to exist in the thick layers of caesium.

Fuchs has compared the results now available for caesium, which extend from 0 to 12,000 A. with a more general theoretical expression than that previously used. The comparison seems to show that the assumption of inelastic scattering of the conduction electrons at the boundaries holds for the thinner films ($t/\lambda < 1/100$) but that at greater thicknesses a considerable proportion of elastic scattering occurs.

Details of these calculations and of the comparison will be published elsewhere in the near future.

§ 7. AGGREGATION IN OTHER METAL FILMS

The idea that agglomeration of the metal might be responsible for the unusually high, or even infinite resistance of thin layers is not new; and its existence has received definite experimental proof in a large number of cases. We may quote, among others, the observations of Estermann[15] (ultra-microscopic examination of thin silver films), Fukuroi[16] (mercury, cadmium and zinc films deposited at 90° K. Optical evidence for agglomeration), Reinders and Hamburger[2] (silver deposited at room temperatures), Cosslett[17] (indium at liquid air temperatures), Andrade and Martindale[18] (sputtered silver films heated subsequently to about 600° K.). But in all previous work, except the last mentioned, the agglomeration has either been rapid and complete so that its intermediate stages could not be observed, or where resistance measurements were also attempted the structure of the films may have been marred by so many other extraneous factors that the primary role of the agglomeration process was obscured. The interest of these experiments on the alkali metals is that the process can apparently be followed in slow motion and under complete control. Moreover, the observation that mere alteration of the surface condition of the substrate without any other change in the experimental conditions can alter the specific resistance of the films by factors of 10^5 or more certainly suggests that the differing results of previous workers may be explicable in terms of a greater or less degree of agglomeration of their films. In fact, we may make the reasonable hypothesis that in all those cases where no electrical conductivity occurs until several atomic layers have been deposited a grained structure is responsible, the agglomeration in these cases being so rapid that with ordinary rates of evaporation no continuous film can be formed in the early stages of the process.

Various other hypotheses have been made to explain the experimental facts. Perucca[19], for example, suggests that all normal metals show anomalously high resistivity in the neighbourhood of a free surface. Thin films would thus show an abnormally high resistance owing to their large surface compared with their volume. There is no theoretical warrant for this belief, and no other experimental evidence to support it.

Zahn and Kramer[20, 21] similarly have proposed upon the basis of certain experimental results that an amorphous non-conducting layer of metal may be put down under certain circumstances. Their experimental results are certainly striking; but again, there is no experimental reason to suppose that thin metallic films are even amorphous except in the case of antimony, and even if the films were amorphous, they would presumably show no higher resistivity than that of a melted metal.

It seems preferable on this account to exhaust the possibilities of the agglomeration hypothesis before looking elsewhere; and the following remarks tend to show that it may play an important role even at very low temperatures of deposition.

When we attempt to apply to other metals the simple picture already advanced to explain the alkalis, the immediate objection arises that nothing is known of the nature and hence the magnitude of the surface energy E_2, and that therefore the

onus of explaining any experimental result can always be thrown upon E_2. We can overcome this objection to some extent, and incidentally get a somewhat clearer picture of the process of formation of evaporated films, by examining in closer detail the processes which take place in putting down the early atomic layers upon the substrate.

Let us first examine from a purely energetic point of view whether or not a layer of atoms approximately monomolecular would be inherently stable. Imagine two possible configurations of the metal upon the substrate. In the first (I) the atoms are supposed to be uniformly dispersed on the substrate; in the second (II) they are gathered up into a globule or agglomerate of small surface. Let L be the latent heat of evaporation of a metal atom from the surface, in electron volts, and L_{metal} the latent heat of evaporation from the metal. Then if $L < L_{\text{metal}}$ the state II or agglomerated form is the one with the lower energy. If $L > L_{\text{metal}}$ state I or the dispersed form has the lower energy. Thus a monolayer will be inherently stable if $L > L_{\text{metal}}$ and inherently unstable if $L < L_{\text{metal}}$.*

Now values for the latent heat of evaporation of metals from glass surfaces have been obtained in a few cases. Examples are given in the table below:

Table 2

Experimenter	Metal and surface	L (k.cal./ g. atom)	L (eV.)	L_{metal} (k.cal./ g. atom)	L_{metal} (eV.)
Estermann[23]	Cd on glass	3·5	0·152	28	1·21
,,	Cd on Cu	3·0	0·130	28	1·21
,,	Cd on Ag	5·0	0·217	28	1·21
,,	Hg on Ag	2·5	0·109	18·5	0·80
Cockcroft[24]	Cd on Cu / Cd on Ag	5·7	0·247	28	1·21

The values of L given above represent the heat of evaporation of an atom from a dilute layer plus the heat of dissociation of a doublet upon the surface. L is therefore an upper limit for the latent heat of evaporation from a dilute layer. In all the above cases L_{metal} is about seven times larger than L and the agglomeration of a dilute layer is energetically possible. Now we were considering the general case of a layer which may approach monomolecular thickness. Although it is true that L will vary with the concentration of the layer it is unlikely that it can increase much† with θ (the fraction covered) and it is practically impossible that it should increase by a factor of seven. So a layer of any concentration will be energetically unstable.

The alkalis on clean glass have not yet been systematically investigated from this point of view. But the observation of Ives[27] and the experiments of Lovell[28] show that a clean glass surface placed in an evacuated enclosure filled with the saturated

* De Boer[22] has previously pointed out that a high latent heat of evaporation for the adsorbed substance in bulk will favour agglomeration.

† Langmuir and Taylor[25] find that the latent heat of evaporation of neutral atoms from the surface actually falls from 2·83 volts at $\theta = 0$ to 1·77 volts at $\theta = 1$. J. K. Roberts[26] (H on W) shows that in this case the latent heat may somewhat more than double from $\theta = 0$ to $\theta = 1$.

vapour of the alkali metals rapidly becomes coated with an invisible conducting layer of alkali metal which persists even though the glass is raised in temperature above its surroundings. The layer must be nearly monomolecular to conduct at all; and it follows that either the latent heat of evaporation of an atom of the alkali from the glass is greater than its heat of evaporation from the metal surface, in which case the glass will be completely covered, or, if less, L cannot differ from L_{metal} by more than a few kT., that is to say, by more than a few hundredths of an electron volt.

It follows that the excess of energy of a dispersed layer over its agglomerated form is either small or is actually negative, and for this reason alone single layers of alkali metal atoms on glass should be more stable than those of cadmium or mercury on the surfaces investigated by Estermann and Cockcroft.

So far we have only discussed whether the agglomeration is energetically possible. Whether it will also in fact take place depends upon the mobility of the atoms over the surface of the glass. Lennard-Jones[29] has given a simple picture of the chief factors which influence this mobility, and we may apply it to the present case.

According to his model an atom on a surface may be regarded as held there by a field of force which has a certain potential. The equipotentials are not however a series of planes parallel to the surface, as we have tacitly assumed till now; a crystal surface, for example, has a periodic structure. On this account regular pockets of low potential will exist upon the surface, and at low temperatures any deposited atoms will vibrate about the minima of these pockets. The latent heat of evaporation of the atom from the surface will then be the energy required to remove an atom from its lowest vibrational level to infinity. But in order to move freely over the surface an atom needs much less kinetic energy than L. In fact, if the atom is given sufficient kinetic energy A for it to surmount the potential barrier between one pocket and the next, it may (so long as it retains the energy) move freely over the surface. Thus, since A is less than L, free motion of the atoms on the surface occurs at temperatures far below those needed to evaporate the atoms from the surface: a well-known experimental fact.

Now A, like L, is dependent both on the nature of the surface and upon the atom concerned. It has been found for metal atoms in a limited number of cases only, and it depends to some extent upon the surface population of the atoms. But we may say in general that L and A increase together. Lennard-Jones[29] estimates that for the particular case of the inert gases upon a surface of alkaline halide A is about $\frac{1}{3}L$. Dilute layers of caesium on tungsten give an activation energy of 0·61 volt and a latent heat of 2·83 volts[25,30]. Bosworth[31] obtains values between 0·14 and 0·57 volt for sodium on tungsten, Frank[32] between 0·2 and 0·6 volt for caesium on tungstic oxide. The latent heats of evaporation of neutral atoms are not known in the latter case but they are certainly greater than 1 electron-volt. We might guess then that the activation energy of an atom on a surface is generally less than a third of the latent heat of evaporation from the surface and may be about a quarter.

On this basis the activation energy of caesium on glass must be at least 0·25 volt whereas cadmium on glass, using Estermann's value for the latent heat, would have an activation energy of only 0·04 volt. This difference will be reflected in a great

difference of mobility in the two cases. Assuming a time of activation of about 10^{-13} second (Lennard-Jones[29]) and a surface temperature of 90° K. in both cases we find that a caesium atom would be activated only once every ten seconds, when it would move a distance of 0·6 A., whereas a cadmium atom would be activated nearly 10^{11} times in one second, would move a total distance of about 200 cm., and would migrate about $\frac{1}{100}$ mm. from its original position in this time.

This estimate is purely illustrative and it is of course very sensitive to the actual values of the activation energy assumed. Nevertheless it does enable us to understand how it may be possible in the case of the alkalis to lay down a second layer of atoms before the atoms in the first layer have moved much from their original positions, whereas in the case of cadmium at the same temperatures rates of deposition quite impracticably rapid would have to be used to do this.

We might therefore classify metallic films into three broad classes depending upon the stability of their first layers. For type I, $L > L_{\text{metal}}$ and the first layer is inherently stable. The classical example of this is caesium atoms on clean tungsten for all values of θ. Perhaps caesium on clean glass also belongs to this group; for this would account for the great stability of the early layers in the experiments we have already described using this particular metal. For type II, $L < L_{\text{metal}}$ but $L \sim 1$ electron volt or more. The activation energy is a few tenths of a volt, agglomeration takes a period of minutes at 90° K. and fairly coherent films can be readily prepared at somewhat lower temperatures of deposition, using deposition rates of the order of a molecular layer in a few minutes. For type III $L < L_{\text{metal}}$, $L \sim 0{\cdot}1$ eV. and the activation energy is only a few hundredths of an electron volt.* Films of type III will show rapid agglomeration even at very low temperatures of deposition and in fact approximate to the two-dimensional gas of Frenkel[33] and Cockcroft[24]. These metals even when deposited at very low temperatures will show very different resistivity-thickness relations from the alkalis. We may imagine the successive stages in the development of a film of this type somewhat as follows, starting from the bare substrate: As deposition proceeds doublets are first formed which gradually accrete more atoms round them, and island patches of metal are formed. During this stage of the process there can be no electrical conductivity since the film consists of flat isolated aggregates joined only by a very dilute phase of two-dimensional gas. As the deposition proceeds the island patches thicken both from condensation at their free surfaces and by shrinking under their very high surface-tension forces. The next stage in the process occurs when the aggregates have become so thick and the curvatures of their free surfaces have been so diminished that the surface forces can produce no further flow in the metal. The aggregates now thicken only slowly from deposition at their upper faces, and continue to grow edgewise by condensation from the two-dimensional gas. At a certain stage they will touch, and conductivity will abruptly begin. After this the film-resistivity should quickly approximate to that of the bulk metal.

Some preliminary results obtained in this laboratory with thin films of mercury-

* Semenoff, Chariton, and Schalnikoff[38] have discussed films of type III from a similar point of view to the above, without reference however to the effect on the electrical conductivity.

on-pyrex certainly suggest that these films are an extreme form of type III even when the deposition takes place at temperatures as low as 20° K. Figure 6 shows a family of {resistivity, thickness} curves, each curve characteristic of a different temperature of the condensing surface. (Deposition rate about 9 A./min. in all cases, but this is subject to correction on calibrating the beam, a difficult matter in the case of mercury). The short vertical marks above each curve show the onset of conductivity. This was remarkably sudden, the resistance falling from an unmeasurably high value greater than 10^{10} ohms to a few thousand ohms within about 15 sec., which corresponded to an increase in nominal thickness of less than a monolayer. At this point in the deposition, when the aggregates first touched, the film rapidly disintegrated if currents greater than a few microamps passed through it.

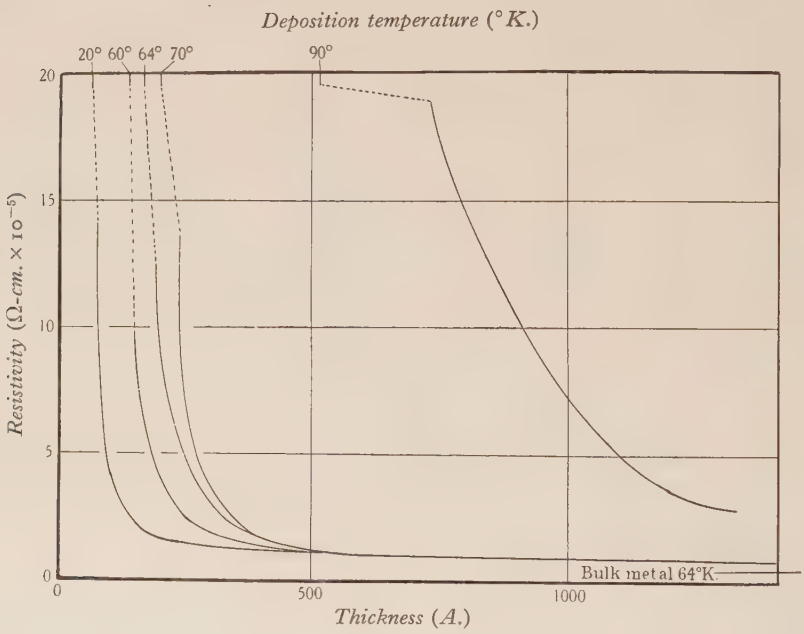

Figure 6.

Figure 7 shows critical thickness plotted against deposition temperature. It will be noticed that there appear to be no signs that by lowering the temperature below 20° K. the critical thickness will much diminish. Thus there appears the surprising suggestion that apparently the atoms of mercury retain their mobility down to very low temperatures. Mercury atoms on pyrex therefore may be similar to helium atoms on lithium fluoride which, according to the theoretical calculations of Lennard-Jones[34], have a finite mobility at all temperatures above absolute zero.

On our picture of the process we should estimate that the critical thickness of the film is about the thickness of an aggregate whose curvatures have so diminished that the surface forces can no longer produce any plastic deformation. Now roughly

speaking the stresses due to surface forces in an aggregate are inversely proportional to its thickness. The critical thickness should therefore give us a measure of the weakness of the metal at that temperature. Although no experiments appear to have been done on single crystals of mercury at these low temperatures, a rough comparison with the results for magnesium[35] single crystals suggests that mercury, which has a low melting point, might begin to alter its mechanical properties rapidly in the region of 80° K., where the rapid rise of critical thickness with temperature does set in. But until further evidence accumulates we must regard this as a speculative guess, particularly since all experiments on the mechanical properties of metal crystals have been carried out with large specimens and not with the microscopic or submicroscope aggregates we have postulated in thin films.

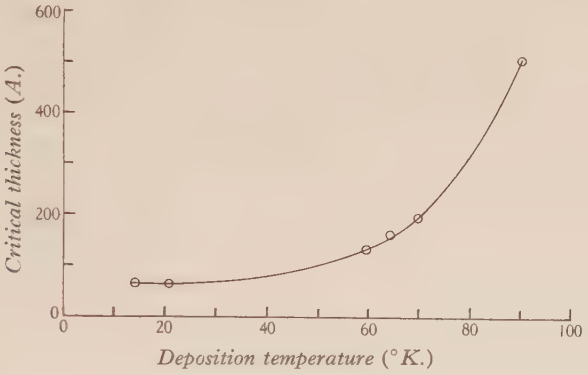

Figure 7.

To summarize the above conclusions: The foregoing discussion suggests that the degree of agglomeration in evaporated films is determined on the one hand by the activation energy of the atom upon its substrate, on the other by the resistance of the metal to plastic deformation, not simply by the melting point of the metal as certain writers have suggested.

§ 8. RECRYSTALLIZATION OF THIN METAL FILMS

Films which agglomerate in their early stages must have a very finely polycrystalline structure which may persist to great thicknesses. The resultant large surface of misfit between the microcrystals may have two effects. First they may increase the resistance of even thick films appreciably above that of the bulk metal; secondly, they introduce a new type of surface energy which may become important when their area becomes large compared with that of the boundaries of the film.

The effect on the resistivity of the film would be to add a *restwiderstand* to the normal resistivity, and on this account even very thick evaporated films deposited at temperatures below that at which recrystallization would occur might show a considerable excess of resistivity over that of the normal metal. It seems possible that in most of the cases where this resistivity excess does not exceed the increase

of resistivity on melting for the pure metal, it may be due to this cause. Annealing should then diminish the resistivity of the films by allowing the surfaces of misfit to relax (recrystallization).

The experiments of Suhrmann and Barth[36] on thick films of copper deposited at 20° K. are consistent with this hypothesis. Annealing at successively higher temperatures lowered their resistivity by diminishing the *restwiderstand* without altering the resistivity change between two definite (lower) temperatures. The highest resistivities observed were nevertheless somewhat in excess of the resistivity change of copper on melting, and it seems on this account possible that occluded gas may have introduced a disorder in the lattice exceeding that produced by melting. Wand[37] has worked out a theory of the relaxation of strain in the lattice which is consistent with his own experimental results, and further experimental work on this point would be valuable.

The effect of this new type of surface energy may account too for the observations of Andrade and Martindale[18] (silver films) as also some recent unpublished observations of Lovell on caesium films. In both cases it was found that thick films could disintegrate so as apparently to increase their free surface and hence their ordinary surface energy. These observations therefore apparently contradict the ideas put forward here that the surface forces control the shape of the film. It is in fact true that in the case of films so thin that the number of atoms in the surfaces is comparable with the total number in the film (say up to 20 atomic layers) ordinary surface forces must predominate. But when thicker films recrystallize it is not at all unlikely that the free-surface energy may increase at the expense of the energy gained from recrystallization and relaxation of the surfaces of misfit.

§9. ACKNOWLEDGEMENTS

I wish to express my thanks to Dr Lovell and Dr Fuchs for permission to publish the preliminary account of their results.

I am also indebted to the Royal Society for permission to reproduce figures 2, 3, 4, and 5 of the present paper (which were originally published in their *Proceedings*) and for the loan of the blocks.

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A STUDY OF THE ELECTRICAL PROPERTIES OF THIN FILMS OF PLATINUM OBTAINED BY CATHODE SPUTTERING IN AIR AND OTHER GASES (He, N_2, O_2 AND H_2)

By A. FÉRY, Collège de France, Paris

For a considerable time attempts have been made to use cathode sputtering in order to obtain thin metallic films so as to study, in particular, the variation of resistivity of these films as a function of their thickness.

All investigators agreed that up to a certain so-called critical thickness the resistivity of the films is a diminishing function of the thickness. Beyond the critical thickness the metal has quite definite physical properties which are those of the *bulk* metal. But for platinum, for example, there are notable discrepancies between the values obtained by different investigators, both for the resistivity of these films at one and the same thickness, and also for the values of the critical thickness. Moreover the resistances obtained in this way were in no way permanent; the adsorption of gas atoms seems to be important. The same uncertainty existed for the temperature coefficients.

I therefore thought that it would be interesting to take up once again the study of the electrical resistance of thin platinum films, with the primary object of getting stable resistances, using first a discharge in air. By taking the same precautions employed in the manufacture of radio valves and, in particular, by getting rid of all traces of water vapour from the apparatus before sputtering (by baking-out in a high vacuum) I was successful in achieving this. The deposits were kept in the apparatus throughout their life. But the platinum so obtained is not ordinary platinum as we shall see in what follows. We shall call it *black platinum*.

I was thus enabled to determine the experimental relationship between the resistivity ρ and the thickness l of these black platinum films. This relationship, which holds between 10 mμ. and 1320 mμ. may be divided into the two curves

$$2 \log (\rho/\rho_0) = 11{\cdot}48 - 0{\cdot}0315\, l$$

and

$$2 \log (\rho/\rho_0) = 3{\cdot}245,$$

where $\rho_0 = 10^{-5}$ ohm-cm. which is the average resistivity of ordinary platinum. These curves are joined up between 237 and 285 mμ. by a very short curved line.

Beyond 285 mμ. the metal may therefore be taken to be compact. But it is nevertheless not ordinary platinum: its resistivity ($4{\cdot}19 \times 10^{-4}$ ohm-cm.) is 42 times higher than the average resistance of bulk platinum. Moreover it appears black. This kind of platinum is adsorbent, has a high resistance, and is catalytic.

Throughout these experiments the temperature of the plate upon which the deposit was received did not increase during the passage of the discharge, for the voltage was low. But if the deposits are heated *in vacuo* their resistance changes. It first increases *reversibly* as the temperature rises, then as soon as the temperature reaches a certain threshold the resistance alters very rapidly and irreversibly, at constant temperature. It diminishes continuously, tending towards a certain limit depending on the temperature of the threshold. By again raising the temperature the same phenomena are reproduced. One thus obtains a series of reproducible transition points 53°, 83°, 97°, 114°, 241° and 340° C. Only at 340° C. do the films have a resistivity between the limits of the tabulated values for normal platinum.

Between any two successive transition temperatures the deposit has quite clearly defined properties. The temperature-coefficient in particular which was $2{\cdot}87 \times 10^{-4}$ for black platinum increases as one approaches the normal bulk metal and finally takes the value $29{\cdot}9 \times 10^{-4}$ very close to that given for the normal metal.

If sputtering is carried out without taking these precautions to avoid heating of the substrate, the form of deposit stable at the temperature reached by the substrate is obtained. This explains the great divergence of the previous results.

The transitions are accompanied by very slight evolution of gas at the first three transition points (the least noteworthy ones). But this evolution of gas is due only to a small adsorption by the deposits (oxygen, nitrogen and oxides of nitrogen) during or after their formation; an adsorption so slight that it can only play a very secondary role in the development of their physical properties.

After transformation into white platinum a new curve is obtained relative to normal platinum. The critical thickness is considerably diminished. It occurs in the neighbourhood of 50 mμ. The "compact" metal has then the resistivity of ordinary platinum. But at very small thicknesses (between 3 and 6 mμ.) this curve is observed to appear to join up again with that of black platinum. The two forms then become indistinguishable.

The properties of the deposits obtained in the simple gases (helium, nitrogen, oxygen, hydrogen) are not clearly defined. During their formation these deposits absorb the gas of the discharge.

At ordinary temperatures after their preparation their resistances fall and tend towards a limit. On heating and holding the temperature at an arbitrarily chosen value, their resistance diminishes again at constant temperature, approaching a new limiting value which is a function of the constant temperature. Parallel with this process the occluded gases are released at a rate which increases the more the temperature is raised. At 500° C. we have still not been able to obtain normal platinum, and the films so obtained are torn up by the evolution of the absorbed gas.

FLUCTUATIONS IN THE RESISTANCE OF THIN FILMS

J. BERNAMONT, Collège de France, Paris

THE study of fluctuations of resistance, begun in 1934[1], has been pursued up to the present time with deposits of graphite[2], with microphone[3] and with metallic deposits[4]. The general results obtained are the following: the mean square of electromotive force averaged over a complete period, which we denote by $\overline{e_\nu^2}$, is approximately proportional to the square of the intensity of the current carried by the conductor, at least in the range of frequencies studied. This range is at present too restricted to allow general conclusions to be drawn; in the experiments with metallic deposits it extends from 96 to 162,000 hertz, while other authors have limited themselves to frequencies from 50 to 10,000. The mathematical investigation of the fluctuations[4] makes it possible to predict that for sufficiently low frequencies $\overline{e_\nu^2}$ ought to be independent of the frequency, and for high frequencies $\overline{e_\nu^2}$ ought to diminish at least as fast as $1/\nu^2$. The curve showing $\log \overline{e_\nu^2}$ as a function of $\log \nu$ ought then to be made up of at least three branches of very different slope, viz. (*a*) a horizontal part for low frequencies; (*b*) for intermediate frequencies a part about which nothing can at present be said from the theoretical point of view, but for which experiment gives a slope of 1; (*c*) for high frequencies a branch with a strong negative slope (at least -2).

The branch (*c*) has been observed with a tungsten deposit;[4] the slope was exactly -2 from 72,000 to 162,000 hertz[4]. Experiments on graphite and microphone[2] show some indications of (*a*).

Since my first observations I have held the opinion that this fluctuation was due to fluctuations in the number of free electrons in the conductor which would give rise to fluctuations in the resistance. A variable electromotive force ought then to appear in the circuit, whose mean square is given by the formula

$$\overline{e^2} = I^2 \overline{\Delta R^2},$$

where ΔR is the instantaneous deviation of the resistance from the mean value.

On the classical theory one can deduce for a cylindrical conductor

$$\overline{e^2} = (I^2 R^2 / n_0 a)\, \overline{\Delta N^2}/N.$$

M. L. Brillouin[5] has shown that this formula follows also from quantum statistics; but the factor $\overline{\Delta N^2}/N$ which is independent of the volume is equal to 1 according to the classical theory but can have another value according to the quantum theory.

To obtain the dependence of $\overline{e^2}$ on ν, one must make a more detailed hypothesis about the mechanism. I have assumed that a free electron has a mean life-time

$\theta = 1/\alpha$. Its collisions with atoms will only alter the direction of its velocity v; and it is only after a very large number of collisions that the electron is captured by an atom and ceases to be free. A group of n free electrons may thus be reduced in number to $ne^{-\alpha t}$ at the end of a time t. Naturally other electrons will be liberated at random during the same interval; this hypothesis leads to the formula

$$\overline{e_\nu^2} = I^2R^2 \frac{\overline{\Delta N^2}}{N} \frac{4\alpha}{\alpha^2 + 4\pi^2\nu^2}.$$

This equation is not in agreement with experiment; but we need not assume that electrons of different velocities have the same life time. If dn is the number of electrons for which the constant α lies in the range $d\alpha$, and if we write

$$\overline{\Delta dn^2}/dn = g$$

then we obtain finally

$$\overline{e_\nu^2} = \frac{I^2R^2}{n_0^2 \alpha} \int_{\alpha_1}^{\alpha_2} \frac{4\alpha g\, dn}{\alpha^2 + 4\pi^2\nu^2},$$

where α_1 and α_2 are the limiting values of α. This formula reproduces the branches (*a*) and (*c*) very well.

Comparison with the experimental branch (*b*) gives us αg as a function of v (for dn is a function of v). But definite conclusions on this subject would be premature.

Actually all experiments of this type have been carried out on conductors of rather badly defined nature. The platinum films have been obtained by M. Féry's method and were very thin. Their thickness was about 40 A., and in M. Féry's experiments conduction only began at 31 A. As one does not know the reason for the absence of conductivity for thinner films the results are rather hard to interpret. It would be desirable to repeat the experiments with films obtained by the method of Appleyard and Lovell and also perhaps with semi-conductors, in such a way as to avoid perturbations which can occur at the contacts where the current enters the film.

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THE MIGRATION AND AGGREGATION OF ATOMS ON SOLID SURFACES

By J. E. LENNARD-JONES, University Chemical Laboratory, Cambridge

§ 1. INTRODUCTION

The interesting experiments of Appleyard and Lovell[1] on the electrical properties of thin films of the alkali metals on pyrex glass direct attention to a number of important theoretical problems concerning the properties of atoms deposited on surfaces. Appleyard* has suggested that when in his experiments a clean surface is bombarded uniformly by metallic atoms, their subsequent behaviour will be conditioned by the surface field of the substratum and by the relative magnitudes of the heat of evaporation from the surface and the heat of sublimation of the metallic atoms from the bulk phase. If the forces of the substratum are strong enough, the metallic atoms may be held in a continuous (more or less uniform) two-dimensional film and its electrical resistance is then of the same order of magnitude as that of the bulk metal. If, however, the cohesive forces between the metal atoms themselves are stronger than those of the substratum, the metallic atoms may tend to aggregate into "islands", which may be many atoms thick. This tendency to aggregation will be opposed by the periodic nature of the surface field and the time taken for the film to reach its most stable configuration will be governed by the rate at which the atoms can migrate over the surface.

This qualitative picture suggests a theoretical investigation of the behaviour of an atom, deposited on a surface, in terms of the interatomic forces between the atoms themselves and between each atom and the surface. The first problem is to determine what is the most stable configuration of the atoms thus deposited. It may be that of a uniform two-dimensional film, or a number of two-dimensional aggregates. On the other hand small three-dimensional crystallites may be more stable than either. This problem is a thermodynamic or statistical one and the answer to it will give the configuration which will eventually be reached after the lapse of a sufficiently long time. In the actual experiments the atoms are deposited uniformly and may or may not be in the configuration which is most stable. The next problem is therefore a dynamic one and is concerned with the length of time it will take the assembly to change from its initial configuration to the most stable one. This will depend on the rate at which atoms can surmount the energy barriers of the periodic field at the surface[2]. In this paper we shall consider some aspects of these two problems.

* The author is greatly indebted to Dr Appleyard for an advance copy of his paper to this conference, with its valuable review of the experimental facts.

§ 2. CRITICAL PHENOMENA IN ADSORBED FILMS

The experiments of Cockcroft[3] and others have shown that when metals are deposited on a surface, they form condensed films if the temperature of the surface is less than a certain critical value. The behaviour of atoms adsorbed on a surface is, in fact, somewhat similar to that of gases and vapours, all of which exhibit critical properties below a certain temperature.

The existence of these critical conditions was discussed by Frenkel[4] who considered the formation of doublets on a surface, held together by an energy greater than that binding them to the surface. He showed that under these conditions a dispersed layer of single atoms would become unstable below certain critical conditions and condensation would occur.

Fowler[5] has recently made a new approach to the problem, basing his work on the treatment of order-disorder phenomena in alloys by Bragg and Williams[6] and Bethe[7]. The energy of an adsorbed atom is assumed to depend not only on the attraction of the surface but also on the number of nearest neighbouring sites occupied by other adsorbed atoms. The assumption was made that the energy of adsorption was a linear function of the number of nearest neighbours. Peierls[8] has shown the relation of Fowler's treatment to Bethe's method and has obtained the critical conditions for atoms adsorbed on a surface when the number of nearest neighbours has any value, Fowler's results being a special case of his.

It may be of interest to give another method of arriving at similar results. We suppose a number of atoms deposited on a perfectly plane surface. At high temperatures and low concentrations these will behave like a two-dimensional gas and binary encounters will alone be of importance. The potential energy of any one atom, referred to an atom at rest in the gas phase as zero, will then be given by

$$\chi=\chi_0+\nu\int_0^\infty \chi_1 e^{-\chi_1/kT}\,2\pi r\,dr \qquad \ldots\ldots(1),$$

where χ_0 is the heat of adsorption of an isolated atom, and χ_1 is the potential energy between any two atoms; ν is the concentration of atoms and is related to θ, the fraction covered by $\theta=\nu S$, where S is the area of each cell into which the surface may be regarded as divided. We see that the equation (1) is similar to the form assumed by Fowler, except that the factor of θ is a function of temperature.

When the concentration becomes high (θ approaches unity), it will not be sufficient to take into account the interaction of pairs only. It will be necessary to calculate the potential of aggregates of atoms. Moreover it will be necessary to work out not only the critical conditions for a two-dimensional phase, but also for the case when the adsorbed atoms can condense together into three-dimensional groups. It is not yet known how the critical conditions for a two-dimensional assembly compare with those of a three-dimensional one. If the critical temperature for two dimensions is higher than that for three, two-dimensional groups may form before three-dimensional ones; but if the critical temperature for two dimensions is lower than that for three, the presumption is that two-dimensional

groups will never form, or if they do, they will very quickly change to the more stable configuration.

An approximate answer to this problem may be obtained by means of a model. We consider a two-dimensional assembly on a perfectly smooth surface. At large densities each atom will always be the immediate neighbour of several others, each of which will exert forces on it and contribute to its potential energy. Although the atom may move from one part of the surface to another, it will always appear to be imprisoned by its environment and will make rapid vibrations about its average path. We may represent this state of affairs by supposing the atom confined to an area, constant in amount and equal to the average area available for each atom, and that within this area there is a region of constant potential energy. The average potential of an atom will, however, depend on the density of the assembly. It will be small for low densities and will gradually fall (to negative values) as the density increases, until a density is reached corresponding to that of a two-dimensional liquid or solid. After this the potential will rise if it is further compressed. So we suppose the potential within a cell to be a suitable function of the area so as to reproduce these features.

The partition function of an atom will then be

$$f = A\frac{2\pi m\,kT}{h^2}\,e^{-\chi(A)/kT}v_z(T) \qquad \text{.....(2),}$$

where A is the area and $\chi(A)$ the potential in the cell, while $v_z(T)$ represents the contribution of the vibration perpendicular to the surface. We assume* that the partition function of the whole assembly can be written as f^N, where N is the number of atoms. Then the free energy of the assembly is

$$F = -NkT\log f \qquad \text{.....(3),}$$

and the two-dimensional pressure P is given by

$$P = NkT\left\{\frac{\partial}{\partial A}\log f\right\}_T$$

$$= NkT\left\{\frac{1}{A} - \frac{\chi'(A)}{kT}\right\} \qquad \text{.....(4).}$$

The potential $\chi(A)$ has the required properties, if it be assumed that

$$\chi(A) = \frac{\lambda}{A^n} - \frac{\mu}{A^m} \qquad \text{.....(5)}$$

with $n > m$.

The critical volume and temperature are given by

$$\left(\frac{\partial p}{\partial A}\right)_T = \left(\frac{\partial^2 p}{\partial A^2}\right)_T = 0 \qquad \text{.....(6).}$$

These lead to the result that

$$kT_c = \alpha\,|\,\chi(A)\,|_{\max.} \qquad \text{.....(7),}$$

where α is a pure number, given by

$$\alpha = m\,(m+1)\,[m\,(m+1)/n\,(n+1)]^{m/(n-m)} \qquad \text{.....(8).}$$

* This step is discussed in a forthcoming paper by the author and A. F. Devonshire on critical phenomena in gases.

A similar result could clearly be obtained for a three-dimensional assembly, using similar methods, viz.

$$kT_c^* = \alpha^* \mid \chi^* (v) \mid_{\max.} \qquad \ldots\ldots(9),$$

where α^* is a similar function of numbers m' and n'. A more detailed and accurate calculation by the author and A. F. Devonshire[9] taking into account the variation of the field within a cell, so that χ is a function not only of v but also of the space coordinates, leads to a similar result for the three-dimensional case and it is found that for the inert gases

$$kT_c = (4/3) \mid \phi \mid_{\max.} \qquad \ldots\ldots(10),$$

where $\mid \phi \mid_{\max.}$ is the energy of dissociation of two atoms. Similar calculations are being made for two dimensions but, in the meantime, it may be said that the indication is that the critical temperature for two-dimensional condensation is lower than that for three dimensions.

The free energy for two dimensions is given by

$$F = -NkT \left\{ \log A + \log (2\pi mkT/h^2) - \frac{\chi (A)}{kT} + \log v_z (T) \right\} \qquad \ldots\ldots(11),$$

and that of a three-dimensional assembly is

$$F^* = -NkT \left\{ \log v + \tfrac{3}{2} \log (2\pi mkT/h^2) - \frac{\chi (v)}{kT} \right\} \qquad \ldots\ldots(12).$$

The difference of the free energies in the two phases is thus (for this model)

$$F^* - F = NkT \left\{ \log \frac{Av_z (T)}{v (2\pi mkT/h^2)^{\frac{1}{2}}} + \frac{\chi (v) - \chi (A)}{kT} \right\} \qquad \ldots\ldots(13).$$

If the potential energy of the adsorbed atom as a function of its distance from the adsorbing surface be represented by a region of constant potential χ_0 for a length z_0, when it changes discontinuously to zero, we get for v_z,

$$v_z = (2\pi mkT/h^2)^{\frac{1}{2}} z_0 e^{-\chi_0/kT} \qquad \ldots\ldots(14),$$

and then

$$F^* - F = NkT \left\{ \log \frac{Az_0}{v} + \frac{\chi (z) - \chi (A) - \chi_0}{kT} \right\} \qquad \ldots\ldots(15).$$

When the volume of an atom in the adsorbed phase Az_0 is comparable with the volume of an atom in the three-dimensional phase v, we see that F^* is less in absolute magnitude than F when

$$\chi (v) < \chi (A) + \chi_0 .$$

Now each of the χ's is the potential energy of a "hole" and is negative, so that we have $\chi = -\mid \chi \mid$ and the condition can be written

$$\mid \chi (v) \mid > \mid \chi (A) \mid + \mid \chi_0 \mid \qquad \ldots\ldots(16).$$

The left hand side may be taken to be the heat of sublimation of the three-dimensional phase and $\mid \chi (A) \mid + \mid \chi_0 \mid$ the heat of adsorption from a condensed two-dimensional phase. This condition is the same as that discussed by Appleyard in his contribution to this discussion, but it is clear that it is only true when the contribution of the vibrational motion to the free energy takes the special form given to it in the above treatment.

The heat of sublimation of a metal is usually much greater than the heat of adsorption of the same metal on to another surface and three-dimensional aggregates are more likely than two-dimensional ones, but the experiments of Appleyard on alkali metals, deposited on pyrex glass, show that in some cases the two energies are comparable in value. For caesium deposited on tungsten special ionic forces are probably brought into play for the first layer owing to the transfer of an electron from an adsorbed atom to the underlying metal and then the two-dimensional phase is unusually stable. These same ionic forces will, however, reduce the value of $|\chi(A)|$ as the film becomes more condensed owing to the mutual repulsion of the dipoles created between caesium and tungsten and eventually $|\chi(v)|$ may be greater than $|\chi(A)|+|\chi_0|$.

§ 3. THE MIGRATION OF ATOMS ALONG SOLID SURFACES

The migration of atoms along solid surfaces has now been investigated by many workers. A summary of work up to 1932 was given by Volmer[10] and since then the technique of measuring the rate of migration has been developed by Langmuir[11], Becker[12], Bosworth[13], and others[14]. In all cases the rate of diffusion is found to vary with temperature according to an exponential law, at any rate approximately, but sometimes, as in the case of caesium on tungsten, the rate of diffusion is also a function of the concentration of atoms in the surface phase.

A theory of surface migration was given by the author[2] in 1932. It was there pointed out that the field in which an atom moves near an adsorbing surface is not two-dimensional in character, as had often been assumed, but was undulatory with a double periodicity similar to that of the lattice. A section of a typical field is shown in figure 1. The continuous lines are sections of the surfaces of equal potential energy. In the immediate neighbourhood of the position of minimum energy the surfaces are closed but eventually they open out and consist of two branches, one above and one below the equilibrium positions.

At low temperatures an adsorbed atom will vibrate about one of the points where the potential energy is a minimum, but, as the temperature of the adsorbing solid is raised, the probability increases that the atom will receive sufficient energy to surmount the potential barrier separating one potential minimum from the next. In order that an adsorbed atom may migrate it must be activated sufficiently to pass over the col between two potential pockets. It was shown that if γ is the number of times per second that an atom is activated to this mobile state and l is the average distance travelled before it is deactivated, the coefficient of diffusion D, defined as usual by the equation

$$\frac{\partial n}{\partial t}=D\frac{\partial^2 n}{\partial x^2},$$

is given by

$$D=\alpha\gamma l^2 \qquad \text{.....(17),}$$

where α is a certain numerical constant of the order of $\frac{1}{2}$ or $\frac{1}{4}$. If the average lateral velocity of an atom during activation is $\bar{v}$ and the average time it remains

activated is τ, while τ^* is the average interval of time between successive activations of the same atom we may write alternatively

$$D = \alpha \bar{v}^2 \tau^2 / (\tau + \tau^*) \quad \ldots\ldots(18a),$$

and if, as in many cases, τ^* is very long compared with τ, we may write

$$D = \alpha v^2 \tau^2 / \tau^* \quad \ldots\ldots(18b).$$

Once D is known from theory or experiment, the bulk diffusion can be calculated by the usual methods[2].

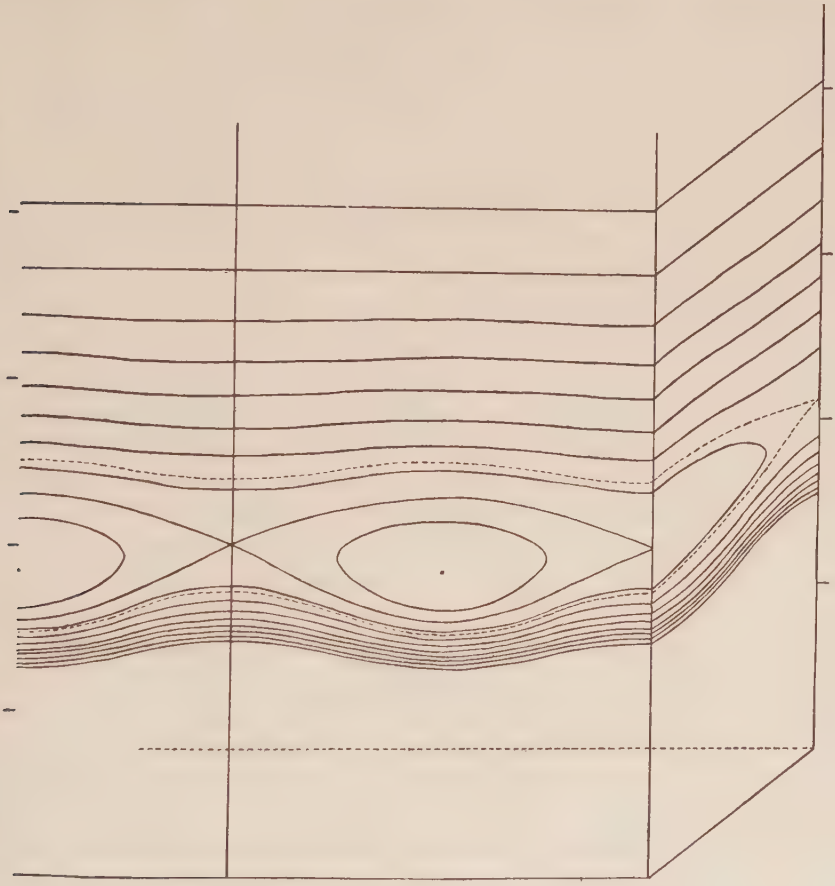

Figure 1. Two cross-sections of the potential field near an adsorbing surface. Continuous lines are sections of equipotential surfaces.

Langmuir in a later paper[11b] gave a special case of (18*b*), based on the assumption that an adsorbed atom is surrounded by four neighbouring sites and that an activated atom hops only to one of them. This leads to the formula

$$D = a^2 / 4\tau^* \quad \ldots\ldots(19),$$

where a is the distance between two neighbouring elementary spaces.

Langmuir also showed that if the time of transit between adjoining sites ($a/\bar{v}$) is not negligible compared with τ^*, then the formula must be modified to

$$D = a^2/4\,(\tau^* + a/v) \qquad \ldots\ldots(20),$$

where $\bar{v}$ is the average velocity parallel to the surface during migration. If τ^* is negligible compared with $a/\bar{v}$, then Langmuir gives

$$D = a\bar{v}/4 \qquad \ldots\ldots(21),$$

which is similar to the formula for a two-dimensional gas when the free path is equal to a, but it is almost certain that for a dilute film the free path would be longer than a, and the formula (21) would have to be modified accordingly.

There remain now the important theoretical problems of calculating the times τ and τ^*. Lennard-Jones and Strachan[15] have obtained theoretical formulae for these quantities for the case when an adsorbed atom is activated from one vibrational state to another for motion perpendicular to the surface and the forces binding the atom to the surface are weak. Since there are forces coupling the adsorbed atom to the underlying solid, the problem is somewhat similar to that of the interaction of coupled oscillators, and energy may be expected to surge to and fro from one to the other. The problem is a little more complicated than that because a solid must be regarded as similar to an assembly of oscillators as in Debye's theory of specific heats. It appears that when an adsorbed atom has been excited to a higher vibrational level, and the temperature is low or (kT) small compared with the energy of excitation, it remains excited for a time of the order of one period of vibration; in a particular example this time was found to about 10^{-12} sec. The important result, however, is that for the range of temperature for which the formula is applicable, the time of excitation is nearly independent of the temperature. For high temperatures the theory indicates a shorter time of excitation inversely proportional to the temperature but the theory is hardly applicable under these conditions.

The formula for the time between successive excitations contains a Boltzmann (exponential) factor corresponding to the energy of activation.

Another mechanism of activation has been considered by Lennard-Jones and Goodwin[16]. When the adsorbing solid is a metal, there will in general be an interaction between the free conduction electrons and the link between solid and adsorbed atom. A simple calculation by classical methods indicates that in a typical case a surface atom may suffer as many as 10^{15} collisions per sec. by the conduction electrons of a metal and since, according to modern views, these are moving with an energy of several volts, they provide an ample reservoir of energy from which adsorbed atoms may absorb energy. The general indication is that an atom will remain excited about 10^{-12} sec. before it falls to the next vibrational level and that this time is nearly independent of the temperature. The advantage of this mechanism is that larger quanta of energy can be communicated to the adsorbed link by a single process and atoms held by chemical bonds (such as hydrogen to a metal) can be thus activated. Several thermal quanta of energy would be required to be communicated to the link *simultaneously* to produce excitation. The corre-

sponding formula for τ^* again contains a Boltzmann term appropriate to the energy of activation.

The author has calculated the dispersal of energy from an activated link also by classical methods, considering a linear array of similar atoms infinite in extent and supposing one of them displaced from its equilibrium position and then allowed to oscillate. It is found that after one complete period the potential energy of each of the links, which was disturbed initially, has fallen to a quarter of its initial value. The dispersal of energy along the chain is thus extremely rapid.

Apart from these mechanisms of deactivation a mobile atom may lose energy also by collision with another mobile atom or by collision with an adsorbed atom in a vibrating state. If the energy of activation for migration is small compared with kT, then most of the atoms will be in the migrating phase and collisions will be numerous. If, however, the energy of activation is large compared with kT, collisions between migrating atoms will be rare, and, if the concentration is not too large so that migration is not prevented by other adsorbed atoms, we may conclude that theory indicates at present that the duration of activation will be nearly independent of temperature.

A relation between the average values of τ and τ^* may be obtained by statistical methods. Let E_s denote an energy level of an adsorbed atom in a vibrating state and E_σ a level in the migrating state (each assumed for the moment to be discrete), and let $b_{s\sigma}$ be the probability per unit time of an activation from E_s to E_σ by the underlying solid. The function $b_{s\sigma}$ includes not only the matrix element of the coupling energy but also the probability that the solid is in a state suitable for the emission of the appropriate amount of energy. Let $b_{\sigma s}$ be the probability of the reverse process. Then in general for statistical equilibrium we must have

$$b_{\sigma s} = b_{s\sigma}\, e^{(E_\sigma - E_s)/kT} \qquad \text{.....(22).}$$

The average value of τ^* is given by

$$\tau^* = \frac{\sum_s \exp(-E_s/kT)}{\sum_s \sum_\sigma b_{s\sigma} \exp(-E_s/kT)} \qquad \text{.....(23),}$$

where the summation in the denominator is over all pairs of states such that one is in the vibrating phase and one in the migrating phase. Similarly

$$\tau = \frac{\sum_\sigma \exp(-E_\sigma/kT)}{\sum_s \sum_\sigma b_{\sigma s} \exp(-E_\sigma/kT)} \qquad \text{.....(24).}$$

Using equation (22), we find that the two denominators are equal and so

$$\frac{\tau^*}{\tau} = \frac{\sum_s \exp(-E_s/kT)}{\sum_\sigma \exp(-E_\sigma/kT)} = \frac{f^*}{f} \qquad \text{.....(25),}$$

where f and f^* are the partition functions relating to the migrating and vibrating phases respectively. This result is quite general whether the levels are quantized or not. Hence the formula for the diffusion coefficient D given in (18a) can be written

$$D = \alpha \bar{v}^2 \tau f / (f + f^*) \qquad \text{.....(26).}$$

In this formula $\bar{v}$ and τ are by definition *average* values, averaged over all migrating states; in fact, v is averaged twice, once over each migrating state and then over all such states. If the average lateral velocity in a state σ of energy E_σ during migration is $\bar{v}_\sigma$, and τ_σ the duration of time spent in this state in each elementary process, the general formula for D is

$$D=\frac{\alpha\Sigma_\sigma \bar{v}_\sigma^{\,2}\tau_\sigma \exp(-E_\sigma/kT)}{(f+f^*)} \qquad \text{.....(27).}$$

where the numerator is a sum over all migrating states. Equations (26) and (27) are equivalent, when $\bar{v}^2\tau$ in (26) is an average value, as just explained.

As an example of the application of the formula (26) we may consider the case when the periodic nature of the surface field is represented by a series of circular potential holes arranged regularly like a lattice. Let the height of the barrier separating these holes be V_0 and let the holes occupy a fraction r of the total surface area A. Then

$$f=A\,(2\pi mkT/h^2)\,e^{-V_0/kT} \qquad \text{.....(28),}$$

and

$$f^*=rA\,(2\pi mkT/h^2)\,(1-e^{-V_0/kT}) \qquad \text{.....(29),}$$

so that for this model

$$D=\alpha\bar{v}^2\tau/\{(1-r)+r\exp(V_0/kT)\} \qquad \text{.....(30).}$$

When V_0 is large compared with kT, this may be written

$$D=(\alpha\bar{v}^2\tau/r)\,e^{-V_0/kT} \qquad \text{.....(31}a\text{),}$$

and when V_0 is small compared with kT, we have

$$D=\alpha\bar{v}^2\tau\Big/\left\{1+r\frac{V_0}{kT}\right\} \qquad \text{.....(31}b\text{).}$$

In the limiting case when V_0 becomes zero, the formula for D is

$$D=\alpha\bar{v}^2\tau=\alpha\bar{v}l \qquad \text{.....(31}c\text{),}$$

where τ is now the time between successive collisions in a two-dimensional gas and l is the mean free path. This is the usual form for the diffusion coefficient for a two-dimensional gas, and simple theories give for α the value of $\frac{1}{2}$.

As an example of the application of formula (31a), we may examine the experimental results obtained by Bosworth[13] for the migration of sodium atoms along a tungsten surface. Bosworth shows that his observations can be represented by the formula

$$D=aT^{\frac{1}{2}}\,e^{-b/T}$$

and from his figures it may be deduced that $b=2750°$, which is equivalent to an energy of activation V_0 of 5500 cal./gram-atom or 0·24 eV. He does not give the value of a but it appears to be $(5{\cdot}64)\ 10^{-3}$, and comparison with the theoretical formula gives

$$\alpha\bar{v}^2\tau/r=(5{\cdot}64)\ 10^{-3}\ T^{\frac{1}{2}}.$$

Taking τ to be 10^{-13} sec. and α/r to be unity, we then get $\bar{v}=(2{\cdot}4)\ T^{\frac{1}{4}}\ 10^5$ cm./sec and the free path ($l=\bar{v}\tau$) at room temperature is 10^{-7} cm. or about three or four

times the length of a unit cell. A rough calculation gives the frequency of vibration of sodium about its position of equilibrium on the surface to be about 2.10^{-13} sec., so that τ may be longer than 10^{-13} sec. Taking it to be 10^{-12} sec., which is likely to be an extreme value, the free path comes out at about $3 \cdot 10^{-7}$ cm., the equivalent of about nine unit cells. In any event the results of Bosworth, interpreted in terms of (31*a*) indicate that the free path is only slightly dependent on temperature. The factor which governs the rate of migration is the rate of activation to the migrating state.

Finally it may be mentioned that migration may occur when atoms collide with the surface from the vapour phase. It has been shown[18] that under certain conditions atoms may be diffracted at a surface without loss of energy in such a way that the atom afterwards runs along the surface. It is caught in one of the vibratory levels perpendicular to the surface, but the energy lost in the normal direction is taken up by the lateral motion and it speeds along in a migratory level. This mechanism satisfactorily explains the observations of Frisch and Stern[19] on the anomalous diffraction of helium by certain crystals and the calculations lead to the conclusion that the mean path of these atoms along the surface before being again diffracted into the vapour phase would be as long as 10^{-5} cm. As they are not so diffracted but are lost from the beam (thus producing the observed anomalies), the inference is that these migrating atoms lose energy either as a result of an encounter with an imperfection in the crystal or with an adsorbed atom or by their interaction with the solid and do not travel so far as 10^{-5} cm. This calculation therefore gives us an upper limit to a free path during migration and, as helium is a light atom and likely to migrate further than heavier atoms under similar conditions, we may infer that free paths are much shorter than 10^{-5} cm.

Migration at very low temperatures will not normally occur except at rates which are so slow as to be unobservable, but helium on certain solids appears to be an exception[20]. Owing to the low energy barrier between neighbouring equilibrium positions and the small mass of the helium atom, penetration of the barrier may occur and calculations by quantum methods show that helium atoms may migrate almost like a two-dimensional gas however low the temperature.

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DISCUSSION OF THE PAPERS BY FINCH, APPLEYARD AND LENNARD-JONES

Reported by E. T. S. APPLEYARD

ONE of the important questions discussed was the cause of the negative temperature coefficient of resistance observed in so many thin films but not in the case of the alkali metals.

Dr Lovell gave an account of some preliminary results which he had obtained with thin films of thallium deposited under the same high vacuum conditions already used by him for the alkali metals. In the region of thickness between 20 and 30 A., the resistivity of the films was about 10^4 times that of the bulk metal, and they showed a negative temperature coefficient. But both their resistivity and their temperature coefficients were much below those obtained previously by Cosslett using the similar metal indium in a vacuum of about 10^{-5} mm. of mercury. On this account Dr Lovell believed that the idea of Cosslett that the negative temperature coefficient was in some way due to gas adsorbed or occluded in the film was strongly supported, more especially since he himself had been able to alter both the resistivity and the temperature coefficient of his thallium films by altering their rate of deposition.

Dr de Boer was unable to accept the general explanation of negative temperature coefficients given above. On the experimental side he pointed out that the results he had obtained with molybdenum were quite reproducible in successive experiments. Moreover, certain unpublished results obtained recently in his laboratory with evaporated tungsten films exactly reproduced the results obtained many years ago by Reinders and Hamburger. It seemed to him almost inconceivable that this agreement could be obtained if the residual gas played any important part. Moreover, he had found that the influence of gas upon the resistivity of the films once formed was unimportant except in the case of oxygen, and that even here the influence was not appreciable provided that the films were kept at liquid air temperatures. He adhered to the view that the thin films of molybdenum and tungsten showed a different atomic spacing from those of the bulk metal, at any rate in the early layers, and that as a consequence of this larger spacing (for which, as yet, there was admittedly no other experimental evidence) the thin films behaved like a semi-conductor. The lower conductivity could arise either as a result of the raising of the potential barriers between successive metallic ions, or from a diminished overlapping of the electronic bands; both would be favoured by an increased interatomic spacing. He suggested that a direct experimental measurement of the

distribution of the electrons in the bands (as compared with the distribution in the bulk metal) might be obtained if Skinner's* method of investigating the X-ray emission spectrum were applied to very thin metallic films.

Dr Fuchs remarked that for monovalent metals a very considerable increase in atomic spacing would be necessary to produce the transition from the metallic to the semi-conducting state, for the potential barrier between successive lattice points was not at all sensitive to small increases of spacing.

Dr Klatzow said that some experiments of his own on the electrical resistance of composite caesium films such as are employed in commercial photoelectric practice had led him to believe that (in agreement with the view of Lovell and Appleyard) their high resistivity and negative temperature coefficients were both to be explained in terms of a disintegrated structure. He suggested that in this case the current was carried across the gaps in the film by cold emission of electrons, i.e. by the movement of electrons across the gaps under the action of the applied electric field (cf. Frenkel, *Phys. Rev.* **36**, 1613 (1930), Ehrenberg and Hönl, *Z. Phys.* **68**, 289 (1931)). On such a theory an increase in the work function would decrease the current. This notion was made more reasonable because on evaporating a thin layer of silver over the composite layer its resistance actually increased. Silver deposition in this way was known quite independently to raise the work function and to diminish the cold-emission of such composite surfaces.

The above discussion clarified the points of difference between the possible hypotheses used to explain the negative temperature coefficient, but no definite conclusions could be drawn as to which one was correct.

Another point discussed was the role of agglomeration in thin films.

Prof. Fowler criticized Dr Appleyard's criterion for agglomeration. He remarked that although it led to the right results when applied at these low temperatures, the general condition for any isothermal process to be possible was of course that the free energy (and not the potential energy) should diminish.

Dr Cockcroft remarked that the values given in table 2 of Dr Appleyard's review should be accepted with reserve since they were obtained in the days before vacuum technique had approached its present level and the surfaces must have been very dirty judged by present standards. This was proved by the fact that the latent heat of evaporation was the same for surfaces of copper, silver and glass. He asked whether the mercury films described in the report were affected by previous heat treatment of the substrate. Dr Appleyard replied that prolonged heat treatment of the type given by Lovell seemed to make no difference whatsoever to the critical thickness or the shape of the resistivity curve, and that this was consistent with the view that mercury-on-pyrex was an extreme case of type-III films.

Dr Skinner observed that zinc, cadmium and mercury seemed to stick with great difficulty to celluloid surfaces. In these cases he had been successful in obtaining films only by saturating the substrate with dirt from the backing vacuum.

Dr de Boer drew attention to the results of some experiments carried out in

* O'Bryan and Skinner, *Phys. Rev.* **45**, 370 (1934). Skinner and Johnson, *Proc. roy. Soc. A* (in Press).

his laboratory on the electrical resistance of evaporated layers of alkali halides coated with adsorbed films of caesium. The halides have a lamellar and labyrinthine structure; the adsorbed layers of caesium on the surfaces of the lamellae are superposed upon each other and so absorb enough light to be visible. It was found that the electrical resistance of such a composite layer changed only very slowly as the adsorption of caesium continued which suggested that agglomeration might be taking place on top of a stable monolayer. Dr Appleyard said that this effect was perhaps somewhat similar to that observed with caesium-on-pyrex. In this case the early layers appeared to be more stable than thicker layers, which suggested that agglomeration here also took place most rapidly with the second, third ... etc. layers, the first layer agglomerating only slowly.

The discussion on agglomeration continued after the paper of Prof. Lennard-Jones. In reply to questions Prof. Lennard-Jones said that he was quite unable to understand how mercury-on-pyrex could possibly show the high mobility at low temperatures suggested by the experimental results. There was no analogy (as Dr Appleyard had implied) between this case and that of helium-on-lithium fluoride previously discussed by him, for the finite mobility at all temperatures above absolute zero obtained with helium depended entirely upon the small mass of the helium atom. It was, of course, possible in principle to calculate the interaction of a mercury atom with a silica surface, and in this way to obtain values for the latent heat and the activation energy, but he would be surprised if the values obtained were low enough to account for the experimental results. A brief discussion then took place on the proper assumptions to be used in calculating the forces in this case.

The general conclusion seemed to be that the role of agglomeration was extremely important in accounting for the high resistance of metal films, and that the criteria for agglomeration put forward by Prof. Lennard-Jones and Dr Appleyard provided a starting point for understanding the process. In spite of this, the paucity of data on the latent heats of evaporation of metals from insulating surfaces prevented anything but the most general qualitative conclusions being drawn in particular cases.

The sputtered films obtained by Dr Féry were also discussed with interest. Prof. Finch mentioned that certain experiments he had performed some time ago were in agreement with the extended investigations of Dr Féry. He too had been able to obtain a catalytic deposit by suitable sputtering methods, and he had found like Dr Féry that the presence of H_2 or H_2 and O_2 in the discharge inhibited the formation of catalytic platinum. He drew attention also to the experimental fact that metal foils heated in air showed a great tendency to form a single crystal, but metallic deposits on an insulating substrate did not.

On Dr Féry's paper Dr Appleyard remarked that it was extremely valuable in enabling us to understand how the black-white transition in platinum could account for the extravagantly different results of previous workers on sputtered films. He remarked that although the temperature coefficient as ordinarily defined diminished greatly on annealing, nevertheless the resistivity change per degree shown in Dr

Féry's work remained fairly constant and approximately the same as for the bulk metal. This could perhaps be accounted for by assuming a diminishing "rest-widerstand".

Dr de Boer then showed another case of an unstable film, in this instance silver evaporated on a liquid air cooled surface. This film on heating suffered an almost explosive disintegration accompanied by a flash of light.

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